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# Comparative study of dehydrogenation of sodium aluminum hydride wet-doped with ScCl<sub>3</sub>, TiCl<sub>3</sub>, VCl<sub>3</sub>, and MnCl<sub>2</sub>

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# ABSTRACT

A comparative study of the dehydrogenation of pure, ScCl<sub>3</sub>-, TiCl<sub>3</sub>-, VCl<sub>3</sub>-, and MnCl<sub>2</sub>-doped sodium alanate is reported. The samples wet-doped with transition metal halides exhibit significant lowering of both first and second dehydrogenation temperatures when compared with the pure sodium alanate. The reduction of the dehydrogenation temperature,  $\Delta T_{dec}$ , is maximum for the VCl<sub>3</sub>-doped alanates: 37 and 55 °C, respectively, for the decomposition steps yielding Na<sub>3</sub>AlH<sub>6</sub> and NaH. Among the transition metal halides, the order in which the decomposition temperature is lowered is Mn < Sc < Ti < V. The reduction in the dehydrogenation temperature of alanates and the observed order are explained by considering the Pauling's electronegativity of Sc, Ti, V, Mn, and Na. Transition metals inductively diminishes the bond strength of the adjacent Al–H bond and renders its easy cleavage to form molecular hydrogen. The transition metal-induced instability shows a quadratic dependence on the electronegativity, in accordance with the Pauling's electronegativity equation.

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ALLOYS AND COMPOUNDS

# 1. Introduction

The development of safe solid-state hydrogen storage materials that exhibit sufficiently fast hydrogenation–dehydrogenation kinetics at ambient temperatures is perceived as the most vexing challenge for the wider utilization of hydrogen fuel. Complex chemical hydrides, such as NaAlH<sub>4</sub>, LiBH<sub>4</sub>, LiNH<sub>2</sub>, etc., possess high hydrogen content, owing to which can exceed the long-term DOE hydrogen storage target [1]. Nevertheless, complex chemical hydrides are well known for their thermodynamic stability, extremely limited, and irreversible kinetics that render them unacceptable for automobile applications [2]. In 1997, Bogdanović and Schwickardi achieved a significant breakthrough by improving the kinetics of alanate dehydrogenation by doping the prototypical alanate, NaAlH<sub>4</sub> with titanium chloride (TiCl<sub>3</sub>) and titanium *ortho*butoxide (Ti-*o*-Bu<sup>*n*</sup>) [3].

A general scheme of reaction between sodium alanate and TiCl<sub>3</sub>, as shown below involves the liberation of hydrogen [4]:

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$$x$$
NaAlH<sub>4</sub> +  $y$ TiCl<sub>3</sub>  $\rightarrow$  ( $x - 3y$ )NaAlH<sub>4</sub>

$$+yTi + 3yNaCl + 3yAl + 6yH_2$$
(1)

According to this reaction, it is clear that in a pre-mixed composition, 3 mol of sodium alanate is rendered unusable for each mole of TiCl<sub>3</sub> used. Additionally, the above scheme indicates separation of Ti and Al phases, while it has been argued that Ti-doped NaAlH<sub>4</sub> produces Al<sub>3</sub>Ti or other Ti-Al alloy phases [5]. This is because the formation of Al<sub>3</sub>Ti from a mixture of Al and Ti is thermodynamically favorable with the free energy change of 136 kJ mol<sup>-1</sup> [6]. Direct doping of NaAlH<sub>4</sub> with Al<sub>3</sub>Ti, indeed, improved its de-/hydriding kinetics suggesting the likelihood of catalysis by Al<sub>3</sub>Ti [7]. Likewise, the X-ray diffraction (XRD) analysis of ball-milled TiCl<sub>3</sub>-doped NaAlH<sub>4</sub> shows evidences of in situ Ti-Al alloy formation [8]. However, the existence of pure Al in zero-valent state has been shown using the photoelectron spectra, which indicates the absence of Al<sub>3</sub>Ti alloy phase [9]. Thus, presently the origin and mechanism of transition metal-mediated alanate dehydrogenation are intensely debated. The application of the transition metal halides other than TiCl<sub>3</sub> and Ti-based compounds is not investigated extensively and is restricted to few studies [10-12]. Resan et al. compared the catalysis by FeCl<sub>3</sub> with that of TiCl<sub>3</sub> and TiCl<sub>4</sub> and found it inferior to the latter [10]. Blanchard et al. found that VCl<sub>3</sub> reduces the LiAlH<sub>4</sub> decomposition temperature by 60 °C, slightly better than  $TiCl_3 \cdot (1/3)(AlCl_3)$ , which reduces

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the temperature by 50 °C [11]. Furthermore, they found that VCl<sub>3</sub> induces less decomposition during ball milling when compared with the Ti-based additive. An extensive study of hydrogen desorption kinetics of various transition metal halides ball-milled with NaAlH<sub>4</sub> is performed by Anton [12]. Moreover, the ball milling of pure NaAlH<sub>4</sub> activates it so as to allow desorption of hydrogen at a significant rate. Using the Vegard's law, it has been observed that cations having a radius in the range of 0.73–0.80 Å should hold the highest potential for enhanced hydrogen desorption rate [12].

In this letter, we compare the kinetic enhancement and degree of dehydrogenation of TiCl<sub>3</sub>-, VCl<sub>3</sub>-, ScCl<sub>3</sub>-, and MnCl<sub>2</sub>-doped sodium aluminum hydride with that of un-doped pure sodium alanate. The alanates are wet-doped using condensed-phase reaction involving predetermined quantities of alanate and transition metal halides in tetrahydrofuran (THF) medium, under moisture-free Schlenk tube technique. The dehydrogenation of alanates and evolution of alanate phases are investigated using thermogravimetric and XRD analysis of the samples. The decomposition temperature of transition metal-doped alanates is correlated to the alanate-hydrogen bond strength and shows a quadratic dependence on the electronegativity of the transition metals, in agreement with the Pauling's electronegativity relation.

#### 2. Experimental

#### 2.1. Purification and doping of sodium alanate

TiCl<sub>3</sub>, VCl<sub>3</sub>, MnCl<sub>2</sub>, THF, and *n*-hexane were sure-sealed reagents with purity of 99.95% and were purchased from Aldrich. Sodium alanate of purity 97% was obtained from Aldrich and was purified by re-crystallizing from THF solvent using *n*-hexane. For doping of alanates with transition metals, 20, 25, 10, and 5 mmol of sodium alanate were reacted with 0.5 mmol of TiCl<sub>3</sub>, VCl<sub>3</sub>, 0.25 mmol of MnCl<sub>2</sub>, and 0.1 mmol of ScCl<sub>3</sub>, respectively. The mole ratios corresponding to the used reagents are 2.4 mol% (TiCl<sub>3</sub>) and 2.0 mol% (VCl<sub>3</sub>, MnCl<sub>2</sub>, and ScCl<sub>3</sub>). The reaction was performed at 35 °C for nearly 20h under inert atmosphere using standard Schlenk technique, so as to avoid the contamination of air- and moisture-sensitive chemicals. After the reaction, solution was filtered and traces of solvent in the precipitate were removed by heating the samples at 80 °C under vacuum.

#### 2.2. Characterization of pure and doped alanates

The thermogravimetric analysis of pure and doped alanates was recorded using thermogravimetric analyzer TQ50 under N<sub>2</sub> atmosphere. The TGA was collected using a ramp rate of 5 °C/min. The powder XRD spectra of alanates were recorded using Rigaku D/MAX 2500 X-ray diffractometer equipped with Cu K $\alpha$  radiation source ( $\lambda$  = 0.15418 nm). The morphology of as-purchased and doped alanates was compared using a field emission scanning electron microscope, FESEM (Hitachi S-4700). Fourier transform infrared (FTIR) spectra of the samples were recorded using a Varian FTS 1000 spectrometer, using the dry KBr pellet method.

#### 3. Results and discussion

The morphology of the alanates is displayed in Fig. 1(A), where the panels (a), (b), (c), (d), and (e) represent the FESEM images and EDS of pure, ScCl<sub>3</sub>-, TiCl<sub>3</sub>-, VCl<sub>3</sub>-, and MnCl<sub>2</sub>-doped sodium alanates, respectively. One can see that particle size of alanates becomes finer after the doping. The histograms showing the particle size distributions (PSDs) of pure, ScCl<sub>3</sub>-, TiCl<sub>3</sub>-, VCl<sub>3</sub>-, and MnCl<sub>2</sub>-doped sodium alanates are constructed by sampling several FESEM images and are provided in Fig. 1B(a)-(e). The pure, ScCl<sub>3</sub>-, TiCl<sub>3</sub>-, VCl<sub>3</sub>-, and MnCl<sub>2</sub>-doped sodium alanate particles formed possess broad diameter distribution that peaked at 13.51, 5.01, 8.72, 4.50, and 5.66  $\mu$ m, with a standard deviation,  $\sigma$  = 5.82, 3.39, 4.89, 2.26, and 3.60 µm. EDS of each sample shows the presence of sodium, aluminum, and transition metal dopants such as Sc, Ti, V, and Mn as shown in Fig. 1(a)-(e), respectively. In addition, the major elemental composition present in the EDS profiles were Na and Al in the ratio of approximately 2:3, respectively. We begin our discussion on the dehydrogenation of doped alanates by referring to the thermogravimetric profiles of alanates presented in Fig. 2, where (a), (b), (c), (d), and (e) represent the TGA data of pure, ScCl<sub>3</sub>, TiCl<sub>3</sub>, VCl<sub>3</sub>, and MnCl<sub>2</sub>-doped sodium alanate, respectively. In the inset, the differential of the corresponding profiles are provided. For pure sodium alanate, the onset of the first decomposition occurs at 169.4 °C, much less compared to 187 °C, previously reported by Zhang et al. [13]. The decomposition rate of the first step yielding Na<sub>3</sub>AlH<sub>6</sub> (Eq. (2)), increases dramatically at 196.82 °C and remains constant until 203 °C.

$$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$$
(2)

At 226  $^{\circ}$ C, the TG profile indicates a shift in the rate of decomposition implying the onset of the second decomposition, yielding NaH:

$$Na_3AIH_6 \rightarrow 3NaH + AI + \frac{3}{2}H_2 \tag{3}$$

The amount of hydrogen released in the first step is 1.15 wt.%, which is equivalent to 31% of the theoretical maximum. The second stretch of decomposition that starts at 226 °C continues until 285.6 °C. The derivative of the TG profile suggests four distinct peaks in this temperature range. The peak at 251 °C can readily be ascribed to the phase transition of  $\alpha$ -Na<sub>3</sub>AlH<sub>6</sub> to  $\beta$ -Na<sub>3</sub>AlH<sub>6</sub>, while the 265 °C peak corresponds to the decomposition of Na<sub>3</sub>AlH<sub>6</sub> yielding NaH [3]. In order to confirm the temperature evolution of Na<sub>3</sub>AlH<sub>6</sub> and NaH phases, the XRD spectra of sodium alanate heated to five different temperatures, i.e., RT, 140, 180, 220, and 260 °C are compared in Fig. 3. Initially at room temperature, the XRD spectrum exhibits the characteristic peaks of NaAlH<sub>4</sub>. After subjected to 140 °C, its partial decomposition leads to the formation of Na<sub>3</sub>AlH<sub>6</sub> and Al, which is evident from the XRD spectrum. However, the decrease in intensity of NaAlH<sub>4</sub> peaks indicates the decomposition of partial amount of NaAlH<sub>4</sub> at this stage. At 180 °C the peak at  $2\theta$  = 37° shows a broad feature which matches with the XRD peak positions of both NaAlH<sub>4</sub> and Na<sub>3</sub>AlH<sub>6</sub> (JCPDS file no. 20-1072). Thus, even at 180 °C, the first decomposition of the sodium alanate is apparently incomplete. However, with the further rising of temperature. a slight shift of this peak to lower  $2\theta$  and typical sharpening indicate the completion of the first step of reaction. More importantly, as the temperature increases to 220 °C, the main peaks of NaAlH<sub>4</sub> at  $2\theta = 31.5^{\circ} (103)$  and  $35.5^{\circ} (200)$  disappeared implying the completion of the first decomposition step. Also, very high intensity of the aluminum peak (111) at 220 °C, here, implies that the formed Na<sub>3</sub>AlH<sub>6</sub> partially decomposes yielding Al and NaH. This is not surprising, as in TGA the onset of decomposition is close to 220 °C. The small peak recorded at  $2\theta = 35.26^{\circ}$  (104) matches well with the main peak of aluminum oxide (JCPDS file no. 46-1212), which presumably formed by the oxidation of aluminum when negligible amount of O<sub>2</sub> is present in the reaction medium. The formation of Al<sub>2</sub>O<sub>3</sub> has been previously observed by Herberg et al. using the Al<sup>27</sup> nuclear magnetic resonance spectroscopy [14]. The XRD spectra of transition metal-doped alanates, however, do not show any peak of transition metal halides; which is not unexpected as the metal halides are present only in very small quantities. Nevertheless, the presence of TiCl<sub>3</sub> (JCPDS file no. 18-1396) is clearly evident with a higher dopant concentration of 15 wt.%, shown in Fig. 4.

On adding TiCl<sub>3</sub>, the first decomposition starts prematurely at 139 °C (Fig. 2, trace c). The first decomposition step proceeds until 175.3 °C. The weight loss recorded on completion of the first decomposition is 2.97 wt.%. Note that there is a loss of hydrogen in doped sample according to alanate decomposition Eq. (1), which essentially implies that only (x - 3y) moles of usable alanate per *y* moles of the dopant. Therefore, in the determination of the hydrogen content of doped alanates, we need to account for the weight of the

dopant as well as the partial loss of hydrogen. This is done by determining the weight of the sodium alanate available in the doped sample that remains after the doping reaction, and by replacing Ti by V, Sc, and Mn appropriately in Eq. (1).

The theoretical maximum hydrogen contents that can be released in the first and second decomposition steps of  $TiCl_3$ -doped alanate are given by

$$HS_{1} = \frac{(x - 3y)H_{2}}{(x - 3y)NaAlH_{4} + yTi + 3yNaCl + 3yAl} \times 100$$
(4)

and

$$HS_{2} = \frac{(1/2)(x - 3y)H_{2}}{(x - 3y)NaAIH_{4} + yTi + 3yNaCI + 3yAI} \times 100,$$
 (5)

respectively. Here *x* and *y* are the number of moles of sodium alanate and  $TiCl_3$  used. The maximum hydrogen content that is obtained by the initial decomposition of 20 mmol sodium alanate mixed with 0.5 mmol of  $TiCl_3$ , i.e.,  $HS_1$  is 3.24 wt.%. From the thermal decomposition profile of  $TiCl_3$ -doped alanate, the completion of the first decomposition yielded 2.97 wt.%; implying 90% of the



**Fig. 1.** (A) FESEM and EDS images of pure and doped sodium alanates detailing the morphology, and elemental analysis: (a) pure sodium alanate, (b) ScCl<sub>3</sub>-doped sodium alanate, (c) TiCl<sub>3</sub>-doped sodium alanate, (d) VCl<sub>3</sub>-doped sodium alanate, and (e) MnCl<sub>2</sub>-doped sodium alanate. (B) Provide the histograms of particle size distribution corresponding to the samples of pure sodium alanate (a), ScCl<sub>3</sub>-doped sodium alanate (b), TiCl<sub>3</sub>-doped sodium alanate (c), VCl<sub>3</sub>-doped sodium alanate (d), and MnCl<sub>2</sub>-doped sodium alanate (e). The average diameter of these particles is found to be  $13.51 \pm 5.0$ ,  $5.01 \pm 2.2$ ,  $8.72 \pm 3.5$ ,  $4.50 \pm 2.0$ , and  $5.66 \pm 2.5 \mu$ m.



Fig. 1. (Continued).



**Fig. 2.** Thermogravimetric (TG) profiles of pure and doped sodium alanate performed under N<sub>2</sub> atmosphere. The TG data of (a) pure sodium alanate, (b) ScCl<sub>3</sub>-doped sodium alanate, (c) TiCl<sub>3</sub>-doped sodium alanate, (d) VCl<sub>3</sub>-doped sodium alanate, and (e) MnCl<sub>2</sub>-doped sodium alanate are represented. The data are collected using a temperature ramp of 5 °C/min. The inset displays the differential thermal analysis (DTA) of the samples, where profiles (a), (b), (c), (d), and (e) correspond to the DTA plots of pure and scandium, titanium, vanadium, and manganese chloride-doped sodium alanate, respectively.

theoretical maximum hydrogen content. Comparing this with the hydrogen released from pure alanate suggests an improvement by a factor of three. In the second decomposition step, the maximum content estimated using Eq. (3) is 1.7 wt.%, while experimentally we obtained 1.19 wt.%, indicating the release of 73% of the theoretical content. The total amount of hydrogen released in both steps is equivalent to 4.16 wt.%, which is slightly lower than the amount of hydrogen released by the pure alanate, i.e., 4.43 wt.%. We subsequently estimated the hydrogen contents in ScCl<sub>3</sub>-, VCl<sub>3</sub>-, and MnCl<sub>2</sub>-doped NaAlH<sub>4</sub> by using the actual amount of these halides and replacing Ti in Eqs. (2) and (3) by Sc, V, and Mn, respectively. The results of these estimations are compared in Table 1.

The numbers in the parentheses indicate the lowered decomposition temperature with respect to the pure alanate. The onset of the decomposition temperatures are obtained from the tangents to the TGA profiles.

Comparing the decomposition temperature as well as the actual amount of hydrogen released of pure alanate, it is evident that doping of all four metal halides had catalyzed the alanate decomposition. The decomposition temperature is lowered by up to 51 °C when NaAlH<sub>4</sub> was wet-doped with TiCl<sub>3</sub>, which closely agrees with the previously reported  $T_{dec}$  of Ti-o-Bu<sup>n</sup>-doped sodium alanate [13]. Among the four transition metal halides, we found VCl<sub>3</sub> is best suited in lowering the initial decomposition temperature; which

#### Table 1

comparison of the mydrogen content of pure and doped sourum alanate
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	Maximum capacity		% of H <sub>2</sub> released compared to maximum capacity	
	Eq. (2)	Eq. (3)	First decomposition	First and second decomposition
Pure NaAlH <sub>4</sub>	3.7	1.8	31.1%	80.3%
ScCl <sub>3</sub> -NaAlH <sub>4</sub>	3.3	1.7	89% (26±4°C)	77% (31 ± 5 °C)
TiCl <sub>3</sub> -NaAlH <sub>4</sub>	3.3	1.7	90% (32±4°C)	83% (51 ± 4 ° C)
VCl <sub>3</sub> -NaAlH <sub>4</sub>	3.3	1.7	92% (37±4°C)	78% (55 ± 4 ° C)
MnCl <sub>2</sub> -NaAlH <sub>4</sub>	3.3	1.7	84% (35±4°C)	80% (35±5°C)



Fig. 3. Thermal evolution of XRD patterns of pure sodium alanate collected at RT, 140, 180, 220, and 260  $^\circ\text{C}.$ 

lowers the  $T_{dec}$  of first and second decomposition by up to 37 and 55 °C, respectively. The order in which the initial decomposition temperature is lowered is Mn < Sc < Ti < V.

To understand the transition metal halide-mediated dehydrogenation of sodium aluminum hydride, the mechanism of the alanate decomposition is concisely considered in the following. Initially, the reaction between the NaAlH<sub>4</sub> and metal halide, which leads to the formation of the transition metal alanate,  $M(AlH_4)_3$ (M = Sc, Ti, V) is envisaged:

$$3NaAlH_4 + MCl_3 \rightarrow M(AlH_4)_3 + 3NaCl \downarrow$$
(6)



Fig. 4. XRD pattern of sodium alanate treated with 15 mol% of TiCl<sub>3</sub>. The reaction is performed for 2 h at RT.

The driving force for this reaction is the precipitation of highly ionic NaCl in the THF medium. Furthermore, a qualitative picture of this reaction can be easily developed by utilizing the Pearson's hard soft acid-base (HSAB) concept [15]. The HSAB principle outlines that hard acids react faster with hard bases and form stronger bonds while soft acids react faster with soft bases to form stronger bonds [15]. In the Pearson's scale, hardness of hypervalent transition metal ions, such as Sc<sup>3+</sup> is higher than that of monovalent Na<sup>+</sup> ion ( $\eta$  = 24.6 eV vs. 21.1 eV) [15]. Thus, intrinsically hard complex anion, AlH<sub>4</sub><sup>-</sup> prefers to bond with the transition metal ion and forms transition metal alanate, M(AlH<sub>4</sub>)<sub>3</sub>. Once, the transition metal alanate is formed, its thermal decomposition can be readily understood in terms of the dissociation of Al-H bonds, the pairing of H atoms to form molecular hydrogen and the electronic contribution of transition metals. In Ref. [16], Grochala and Edwards outlined a general dehydrogenation mechanism of alanates. This mechanism involves the dissociation of Al-H bonds and the pairing of four ligated H atoms to form two hydrogen molecules [16]. A simple way to accommodate the electronic contribution of the transition metal counter ions in the cleavage of Al-H bonds is to consider the transition metal electronegativity. The Pauling's electronegativity  $\chi_P$  of transition metals increases from 1.36 to 1.63 as we move across the periodic table from Sc to V (see Table 2). The rising electronegativity of transition metals inductively diminishes the electron density between Al and H, which renders an easy cleavage and forms molecular hydrogen.

This is, in principle, in accordance with the kinetic stabilization of hydrides when hydrogen atoms are substituted with electron donating groups, as observed by Brynda et al. [17]. A correlation between the electronegativity and the bond strength is given by the Pauling's definition of electronegativity [18]:

$$\chi_{alanate} - \chi_H = eV^{0.5} \sqrt{\frac{Ed_{alanate-H} - [Ed_{Al-Al} + Ed_{H_2}]}{2}}$$
(7)

Here  $\chi_{alanate}$  and  $\chi_{H}$  represent the Pauling electronegativity of -MAlH<sub>3</sub> species and H, respectively, while, Ed<sub>Al-H</sub>, Ed<sub>Al-Al</sub> and Ed<sub>H<sub>2</sub></sub> are the bond dissociation energies of Al–H, Al–Al, and H–H, respectively. The electronegativity of transition metal alanates –MAlH<sub>3</sub>,  $\chi_{alanate}$  are determined using the super-atom approximation and employing,  $\chi_{alanate} = [V_c \times \chi_c + \sum_i N_i \chi_i]/N$ , where  $V_c$ , and  $\chi_c$  are

the valence and electronegativity of the central atom in MAIH<sub>3</sub> species.  $N_i$  and  $\chi_i$  are the number and electronegativities of *i*th species attached to the Al, and *N* is the sum of the valence of the

Comparison of the Pauling's electronegativities of ions

Table 2

lon	XΡ	Xalanate
Na <sup>+</sup>	0.93	1.77
AlH <sub>4</sub> -	1.95	
Sc <sup>3+</sup>	1.36	1.83
Гі <sup>3+</sup>	1.54	1.85
V <sup>3+</sup>	1.63	1.87
Mn <sup>2+</sup>	1.55	



**Fig. 5.** (a) Monotonic dependence of first decomposition temperature on the alanate–hydrogen bond strength for pure and transition metal-doped sodium alanate. (b) The quadratic dependence of the first decomposition temperature on the electronegativity difference of MAIH<sub>3</sub> and H, i.e.,  $\chi_{alanate} - \chi_{H}$  is provided.

central atom and the number of substituents connected to the central atom. In Table 2,  $\chi_{alanate}$  estimated using  $V_c = 3$ ,  $\chi_c = 1.61$ ,  $N_H = 3$ ,  $\chi_{\rm H}$  = 2.20,  $N_{\rm M}$  = 1 and the individual electronegativities of Sc, Ti, V, and Mn are presented. Utilizing the group electronegativity values provided in Table 2, we estimate the bond strength of Al-H in transition metal alanates. In Fig. 5(a), the observed monotonic dependence of the Ed<sub>alanate-H</sub> on the decomposition temperature is depicted. This monotonic variation agrees well with Nakamori et al.'s density functional calculations on metal borohydrides [19]. The stability of alanates induced by the difference in the electronegativity  $\chi_{alanate} - \chi_{H}$  takes a quadratic dependence according to Eq. (7). Note that here we neglect the influence of transition metals on the Al-Al dissociation energy and use the bond dissociation energy of 1.93 eV [20]. We do not know the magnitude of uncertainty arising from this assumption; however, we presume that it is small due to typically large inter-atomic separation between Al atoms in transition metal alanates. In Fig. 5(b), the quadratic dependence of first decomposition temperature on  $\chi_{alanate} - \chi_{H}$  is presented, as expected from Eq. (7).

Additionally, the evidence for the weakening of Al–H bond in doped alanates stems from the red-shift of the Al–H vibrational frequency in FTIR spectra. In Fig. 6, we reproduce the FTIR spectra of pure and Ti-doped sodium alanate in the frequency region  $1200-2000 \,\mathrm{cm}^{-1}$ . The broad band which peaks around ~1655 cm<sup>-1</sup>, is the characteristic of Al–H deformation vibrations



**Fig. 6.** The FTIR spectra of pure and TiCl<sub>3</sub>-doped sodium alanate in the region of Al-H stretching vibrations.

[21,22]. In TiCl<sub>3</sub>-doped sodium alanate we observe red-shift of this band by  $\sim$ 20–1635 cm<sup>-1</sup>. This lowering of  $\nu_{Al-H}$  confirms the decreased covalent character of Al–H bond when the samples are doped with TiCl<sub>3</sub> [22].

# 4. Conclusions

To summarize, we compared the dehydrogenation of ScCl<sub>3</sub>, TiCl<sub>3</sub>, VCl<sub>3</sub>, and MnCl<sub>2</sub>-doped sodium alanate with un-doped pure sodium alanate. The doped samples made using wet-doping method in THF indicate the reduction in the initial dehydrogenation temperature by as much as 37 °C and the second dehydrogenation by as much as 55 °C. Among the transition metal halides, the order in which the initial decomposition temperature is lowered is found to be Mn < Sc < Ti < V. The significant decrease in the initial dehydrogenation temperature when V is used, is attributed to the high electronegativity of the metal, which inductively diminishes covalent bond strength of Al-H bond and renders an easy cleavage to form molecular hydrogen. The dopant-mediated decrease in bond strength is, indeed, manifested by a red-shift of Al-H vibrational frequency in FTIR spectra. The instability induced by the transition metal doping shows a guadratic dependence on electronegativity. in accordance with the Pauling's electronegativity equation.

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