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Kinetic Study and Determination of the Enthalpies of Activation of the Dehydrogenation of Titanium- and Zirconium-Doped NaAlH₄ and Na₃AlH₆Tetsu Kiyobayashi,[†] Sesha S. Srinivasan,[‡] Dalin Sun,[‡] and Craig M. Jensen^{*,‡}

National Institute of Advanced Science and Technology, Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan, and Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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The rates of the dehydrogenation of the sodium alanates NaAlH₄ and Na₃AlH₆ doped with 2 mol % Ti or Zr have been measured over the temperature range 363–423 K. NaAlH₄ and Na₃AlH₆ undergo dehydrogenation at equal rates upon direct doping with titanium. However, Na₃AlH₆ arising from the dehydrogenation of Ti-doped NaAlH₄ undergoes dehydrogenation at much slower rates. Rate constants were determined from the slopes of the dehydrogenation profiles. On the basis of Eyring theory, the enthalpies of activation, $\Delta H^\ddagger$, for the dehydrogenation reactions were determined to be $\sim 100 \text{ kJ}\cdot\text{mol}^{-1}$ for both Ti-doped NaAlH₄ and Na₃AlH₆ and $\sim 135 \text{ kJ}\cdot\text{mol}^{-1}$ for both Zr-doped NaAlH₄ and Na₃AlH₆. These results suggest that the dehydrogenation reaction pathways are highly sensitive to the nature and distribution of the dopant but not to differences in the Al–H bonding interactions in [AlH₄][−] and [AlH₆]^{3−} complex anions. Furthermore, we conclude that the kinetics are probably influenced by processes such as nucleation and growth and/or range atomic transport phenomenon.

Introduction

The development of high-performance hydrogen carriers is becoming increasingly important with the approach of practical, hydrogen-powered vehicles and electronic devices. Over the past several decades, metal hydrides have been utilized in limited applications as hydrogen storage materials. However, a “holy grail” material having both a high hydrogen capacity ($\geq 5 \text{ wt } \% \text{ available hydrogen}$)¹ and rapid hydrogen cycling kinetics at low temperatures has not been attained despite the considerable research efforts that have been concentrated on MgH₂ and a variety of interstitial hydrides.² A number of complex hydrides have considerably high hydrogen capacities. However, until recently, they were precluded from consideration as potential hydrogen storage materials due to their slow dehydrogenation kinetics and poor reversibility. This thinking was changed by the finding that charging NaAlH₄ with a few mole percent of selected transition metal dopants significantly enhances the kinetics of the dehydrogenation process and renders it reversible in the solid state under moderate conditions.^{3,4} This breakthrough has been followed by a great deal of effort to develop alanates as practical hydrogen storage materials.^{5–23} However, the mechanism by which the dopants enhance the dehydrogenation of NaAlH₄ remains an enigma. An understanding of the mechanistic role of the dopants would aid the development of alanates that are suitable for practical applications.

The present study was conducted to obtain quantitative information about the effect of titanium and zirconium dopants

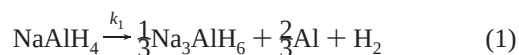
on the dehydrogenation of NaAlH₄ and Na₃AlH₆. We have carried out systematic kinetic measurements over the temperature range 363–423 K and interpreted the resulting dehydrogenation profiles. This information has provided us with insights into the dehydrogenation mechanisms of NaAlH₄ and Na₃AlH₆.

Experimental Section

Materials. Titanium *n*-butoxide, Ti(OBu^{*n*})₄, and zirconium *n*-propoxide, Zr(OPr^{*n*})₄, were obtained from Aldrich Chemical Inc. and used as received. Sodium aluminum hydride, NaAlH₄, was obtained from Albemarle Corp. and recrystallized from tetrahydrofuran prior to use. NaAlH₄ was doped with 2 mol % Ti(OBu^{*n*})₄ or Zr(OPr^{*n*})₄ according to the published procedure.^{5,14}

Kinetic Measurements. The dehydrogenation studies were carried out using an automated Sieverts' type apparatus (LESCA Co), which allowed for the accurate volumetric determination of the amounts of hydrogen evolved. Rapid heating of the sample to the desired temperature was accomplished by immersing the sample reactor into a silicon oil bath (accuracy of $\pm 1 \text{ K}$) preheated to a given temperature. Dehydrogenation was performed against a back pressure of 0.1 MPa in a fixed volume.

Theory of Data Analysis. The dehydrogenation of NaAlH₄ is composed of a two-step process seen in eqs 1 and 2.



Assuming these reactions to be first-order and independent, the differential form of the rate equation is

* Corresponding author. Phone: 1-808-956-2769. Fax: 1-808-956-5908. E-mail: jensen@gold.chem.hawaii.edu.

[†] National Institute of Advanced Science and Technology.

[‡] University of Hawaii.

$$\frac{dN_A(t)}{dt} = -k_i N_A(t) \quad (A = \text{NaAlH}_4, \text{Na}_3\text{AlH}_6; i = 1, 2) \quad (3)$$

The solution of eq 3 gives

$$-k_i t = \ln \left(\frac{N_A(t)}{N_A^0} \right) \quad (4)$$

where k_i is the reaction rate constant and $N_A(t)$ and N_A^0 are the moles of the substance A present at times t and $t = 0$, respectively. It is appropriate to substitute $N_{\text{H}_2}(t)$ for $N_A(t)$ in eq 4 because moles of hydrogen, $N_{\text{H}_2}(t)$, rather than $N_A(t)$ were directly determined in our experiments. In terms of the stoichiometric factors of reactions in eqs 1 and 2, we obtain the relations between $N_{\text{H}_2}(t)$ and the rate constant k_i as

$$-k_1 t = \ln \left(1 - \frac{N_{\text{H}_2}(t)}{N_{\text{NaAlH}_4}^0} \right) \quad (5)$$

for the dehydrogenation of NaAlH₄ and

$$-k_2 t = \ln \left(1 - \frac{2N_{\text{H}_2}(t)}{3N_{\text{Na}_3\text{AlH}_6}^0} \right) \quad (6)$$

for that of Na₃AlH₆.

When the reactions in eqs 1 and 2 are treated as consecutive first-order reactions, the simultaneous differential equations

$$\begin{aligned} \frac{dN_{\text{NaAlH}_4}(t)}{dt} &= -k_1 N_{\text{NaAlH}_4} \\ \frac{dN_{\text{Na}_3\text{AlH}_6}(t)}{dt} &= -k_2 N_{\text{Na}_3\text{AlH}_6} + \frac{1}{3} k_1 N_{\text{NaAlH}_4} \end{aligned} \quad (7)$$

yield the solution

$$\frac{N_{\text{NaAlH}_4}(t)}{N_{\text{NaAlH}_4}^0} = \exp(-k_1 t) \quad (8)$$

and

$$\frac{N_{\text{Na}_3\text{AlH}_6}(t)}{N_{\text{NaAlH}_4}^0} = \frac{1}{3} \frac{k_1}{k_1 - k_2} \{ \exp(-k_2 t) - \exp(-k_1 t) \} \quad (9)$$

by applying the initial condition $N_{\text{Na}_3\text{AlH}_6}^0 = 0$. For the same reason as mentioned above, $N_{\text{H}_2}(t)$ is substituted for $N_{\text{NaAlH}_4}(t)$ and $N_{\text{Na}_3\text{AlH}_6}(t)$ in eqs 8 and 9. Thus the relation between $N_{\text{H}_2}(t)$ and the rate constants k_1 and k_2 is obtained,

$$\begin{aligned} \frac{N_{\text{H}_2}(t)}{N_{\text{NaAlH}_4}^0} &= \left\{ 1 - \frac{k_2}{2(k_1 - k_2)} \right\} \{ 1 - \exp(-k_1 t) \} + \\ &\quad \left\{ \frac{k_1}{2(k_1 - k_2)} \right\} \{ 1 - \exp(-k_2 t) \} \end{aligned} \quad (10)$$

The first term on the right-hand side of eq 10 is the contribution from the dehydrogenation of NaAlH₄, and the second term is that of Na₃AlH₆.

According to the Eyring theory,²⁴ the relation between the rate constant k_i and the Gibbs free energy of activation $\Delta G^\ddagger$ is given by

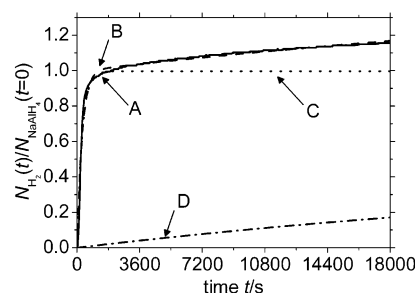


Figure 1. Dehydrogenation of Ti-doped NaAlH₄ at 423 K. (A) Experimental. (B) Theoretical: total (eq 10). (C) Theoretical: contribution from the dehydrogenation of NaAlH₄ (first term on the right side of eq 10). (D) Theoretical: contribution from Na₃AlH₆ (second term on the right side of eq 10).

$$k_i = \kappa \frac{k_B T}{h} \exp \left(-\frac{\Delta G^\ddagger}{RT} \right) \quad (11)$$

where κ is the transmission coefficient, k_B is the Boltzmann constant, h is Planck's constant, T is the absolute temperature, and R is the gas constant. Assuming that κ is independent of the temperature, substituting $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, where $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are respectively the enthalpy and entropy of activation, into eq 11 and rearranging and taking the logarithm gives

$$\ln \left(\frac{k_i}{T} \right) = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \text{constant} \quad (12)$$

Results and Discussion

The overall dehydrogenation profile of NaAlH₄ doped with 2 mol % Ti(OBuⁿ)₄ (Ti-doped NaAlH₄) is seen in Figure 1. The solid line represents the hydrogen evolution $N_{\text{H}_2}(t)$ from Ti-doped NaAlH₄ at 423 K. The profile is composed of two portions: a rapid reaction ($0 \leq t/s \leq 1000$) followed by a slow reaction ($1000 \leq t/s$). Obviously, the first reaction corresponds to the dehydrogenation of NaAlH₄ (eq 1) and the second to the dehydrogenation of Na₃AlH₆ (eq 2). The broken line in the figure shows the close simulation of the profile that was obtained by using eq 10 and values of $k_1 = 3.5 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 2.3 \times 10^{-5} \text{ s}^{-1}$. These rate constants confirm earlier observations that the first dehydrogenation reaction in the stepwise dehydrogenation of Ti-doped NaAlH₄ is much faster than the second.^{5,7,11,15,20,22} In the case of NaAlH₄ doped with 2 mol % Zr(OPrⁿ)₄ (Zr-doped NaAlH₄), the second step is so much slower than the first one that the rate constant, k_2 , could not be determined within a practical time frame. A priori, these results suggest that both the titanium and zirconium dopants provide a much more pronounced intrinsic kinetic enhancement to the first dehydrogenation reaction. However, further experiments, described below, have shown that this is not the case. Although the experimental profile is closely simulated by eq 10 at 423 K, it deviates significantly from the model at temperatures lower than 383 K. This is apparently due to kinetic complications imposed processes not considered in eq 10 (i.e., nucleation and growth or atomic diffusion) that are likely to limit this solid state transformation at the lower temperatures. To clarify the kinetic constraints on the dehydrogenation process, we decided to determine the rate constants k_1 and k_2 of eqs 1 and 2 individually through independent measurement of the dehydrogenation kinetics of the Ti- and Zr-doped NaAlH₄ and Na₃AlH₆.

Na₃AlH₆ was prepared through dehydrogenation of NaAlH₄ in a 350 mL stainless steel reactor at 480–490 K for 3 h

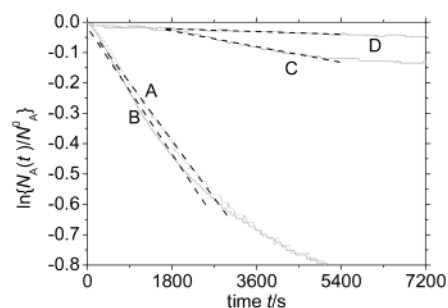


Figure 2. Comparison of the dehydrogenation profiles at 383 K of (A) Ti-doped NaAlH₄; (B) Ti-doped Na₃AlH₆; (C) Zr-doped NaAlH₄; and (D) Zr-doped Na₃AlH₆.

TABLE 1: Dehydrogenation Rate Constants (k/s^{-1}) of Ti- and Zr-Doped NaAlH₄ and Na₃AlH₆

T/K	Ti-doped		Zr-doped	
	NaAlH ₄	Na ₃ AlH ₆	NaAlH ₄	Na ₃ AlH ₆
363	2.3×10^{-5a}		1.3×10^{-6}	
373	2.0×10^{-4a}	7.7×10^{-5}	6.6×10^{-6}	
383	2.4×10^{-4a}	2.6×10^{-4}	3.2×10^{-5}	4.5×10^{-6}
393	4.8×10^{-4}	5.0×10^{-4a}	8.6×10^{-5}	1.4×10^{-6a}
403	1.1×10^{-3a}	1.1×10^{-3}	2.1×10^{-4}	2.9×10^{-5a}
413	2.4×10^{-3a}	2.6×10^{-3a}	4.7×10^{-4}	1.1×10^{-4a}
423	4.8×10^{-3}	3.6×10^{-3}	8.7×10^{-4}	2.8×10^{-4a}

^a Average of two determinations.

according to the procedure of Ashby.²⁵ Analysis of the product by X-ray diffraction confirmed it to be a mixture of Na₃AlH₆ and Al with no traces of NaAlH₄. Measurement of the amount of hydrogen released during heating also verified that the reaction seen in eq 1 proceeds to completion.

Figure 2 compares the dehydrogenation profiles of Ti- and Zr-doped NaAlH₄ with those of Ti- and Zr-doped Na₃AlH₆ at $T = 383$ K. Determination of the slopes of the dehydrogenation profiles (indicated by the broken lines in Figure 2) during the acceleratory period gives the rate constants²⁶ k_1 and k_2 in terms of eq 4: $k_1 = 2.4 \times 10^{-4} s^{-1}$ and $k_2 = 2.6 \times 10^{-4} s^{-1}$ for Ti-doped hydrides; and $k_1 = 3.2 \times 10^{-5} s^{-1}$ and $k_2 = 4.5 \times 10^{-6} s^{-1}$ for Zr-doped hydrides. Thus the dehydrogenation of Na₃AlH₆ that is directly doped with Ti or Zr undergoes dehydrogenation at much faster rates than those observed for the hexahydride arising from the dehydrogenation of doped NaAlH₄. Remarkably, the rates observed for directly Ti-doped Na₃AlH₆ match those of Ti-doped NaAlH₄. However, hexahydride that is directly doped with Zr undergoes significantly slower dehydrogenation than Zr-doped NaAlH₄.

Kinetic measurements were carried out over temperature ranges of 363–423 K for Ti- and Zr-doped NaAlH₄, 373–423 K for Ti-doped Na₃AlH₆, and 383–423 K for Zr-doped Na₃AlH₆. To check the reproducibility and the reliability of the data, the measurements were repeated twice for some temperatures using different batches of hydride. The dehydrogenation rates of Ti-doped NaAlH₄ and Na₃AlH₆ were consistently found to be much higher than those of the Zr-doped hydrides. The obtained rate constants are summarized in Table 1. The activation enthalpies, $\Delta H^\ddagger$, of dehydrogenation were determined from the Eyring plots ($\ln(k/T)$ vs $1/T$) shown in Figure 3. The values derived for $\Delta H^\ddagger$ are summarized in Table 2. Although the standard deviations are large, it can be concluded that the activation enthalpies of dehydrogenation of Ti-doped NaAlH₄ and Na₃AlH₆ are lower than those of the Zr-doped hydrides. For both the Ti- and Zr-doped hydrides, the activation enthalpies of NaAlH₄ and Na₃AlH₆ are comparable: i.e., $\Delta H^\ddagger$ (Ti-doped

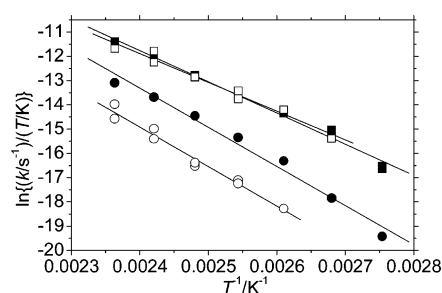


Figure 3. Eyring plots of rate constants for the dehydrogenation of (A) Ti-doped NaAlH₄ ■; (B) Ti-doped Na₃AlH₆ □; (C) Zr-doped NaAlH₄ ●; and (D) Zr-doped Na₃AlH₆ ○.

TABLE 2: Enthalpies of Activation, $\Delta H^\ddagger$, of Ti- and Zr-Doped NaAlH₄ and Na₃AlH₆ (in kJ per mol)

	Ti-doped	Zr-doped
NaAlH ₄	100 ± 7	134 ± 16
Na ₃ AlH ₆	99 ± 13	135 ± 17

NaAlH₄) $\approx \Delta H^\ddagger$ (Ti doped Na₃AlH₆) ≈ 100 kJ·mol⁻¹ and $\Delta H^\ddagger$ (Zr-doped NaAlH₄) $\approx \Delta H^\ddagger$ (Zr doped Na₃AlH₆) ≈ 135 kJ·mol⁻¹.

Conclusions

We have observed that both NaAlH₄ and Na₃AlH₆ undergo dehydrogenation at nearly equal rates directly following mechanical doping with titanium. This finding was quite unexpected, as the Na₃AlH₆ arising from the initial dehydrogenation of Ti-doped NaAlH₄ undergoes dehydrogenation at much slower rates. Thus Ti doping does not innately enhance the dehydrogenation of NaAlH₄ to a greater extent than Na₃AlH₆. Instead it seems plausible that the dehydrogenation of doped NaAlH₄ yields Na₃AlH₆ in which the Ti dopant is not properly distributed for the maximum enhancement of the dehydrogenation of the hexahydride. Our finding that Ti-doped NaAlH₄ and Na₃AlH₆ undergo dehydrogenation at the same rates clearly indicates that the dehydrogenation kinetics are insensitive to variation in the Al–H bonding interactions and are probably influenced by processes such as nucleation and growth or the diffusion of atoms and molecules. These processes may be less important in determining the dehydrogenation kinetics of Zr-doped NaAlH₄ and Na₃AlH₆, as, unlike the Ti-doped materials, directly Zr-doped Na₃AlH₆ undergoes dehydrogenation at significantly different rates than Zr-doped NaAlH₄.

At high temperatures (ca. 423 K) the two-step dehydrogenation of Ti-doped NaAlH₄ to NaH is well represented by a consecutive, first-order reaction kinetics given by eq 7. However, at temperatures lower than 383 K, the dehydrogenation kinetics deviate significantly from this model. This observation provides further confirmation that processes other than the breaking of Al–H bonds in the complex anions play significant roles in determining the rates of dehydrogenation of these materials at lower temperatures.

We have found excellent agreement in the values determined for the activation enthalpies of the dehydrogenation of NaAlH₄ and Na₃AlH₆ with the same dopant (Ti doped ≈ 100 kJ per mol and Zr doped ≈ 135 kJ per mol). This suggests that the dehydrogenation mechanisms of Ti- and Zr-doped NaAlH₄ and Na₃AlH₆ all involve similar reaction pathways in which the dominant energetic consideration is the positioning of dopants rather than the strength of Al–H bonding interactions. In situ X-ray diffraction⁸ and scanning electron microscopy¹⁷ studies have shown that the phases arising from the dehydrogenation of Ti-doped NaAlH₄ are composed of large crystallites with

sizes greater than 100 nm. These findings indicate that processes must be operating in which the constituent metal atoms are transported over a long range. Interestingly, the values of $\Delta H^\ddagger$ that we have determined in this study are close to the value reported for the self-diffusion activation energy of metallic aluminum of $142 \text{ kJ}\cdot\text{mol}^{-1}$.²⁷ This suggests that the rate-determining step in the dehydrogenation of the doped aluminates at lower temperatures may also be a long-range atomic transport phenomenon.

Studies currently in progress of the rehydrogenation kinetics should reinforce our conclusions and perhaps provide further insight. Additionally, microscopic studies of the dehydrogenation reactions based on the knowledge obtained from our macroscopic observations should elucidate the details of the reaction mechanism(s) and function of dopants.

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References and Notes

- (1) Gravimetric hydrogen density targets of 5.0, 6.0, and 5 wt % have been set by the Japanese government, WE-NET project (<http://www.ena.or.jp/WE-NET>), the International Energy Agency (<http://hydropark.ca.sandia.gov/iea.html>), and the U.S. Department of Energy (<http://www.eere.energy.gov/hydrogenandfuelcells/mission>), respectively.
- (2) Bowman, R. C.; Fultz, B. *MRS Bull.* **2002**, 27, 688.
- (3) Bogdanovic, B.; Schwickardi, M. *J. Alloys Compd.* **1997**, 253–254, 1.
- (4) Bogdanovic, B.; Schwickardi, M. International Patent WO97/03919, 1997.
- (5) Jensen, C. M.; Zidan, R.; Mariels, N.; Hee, A. G.; Hagen, C. *Int. J. Hydrogen Energy* **1999**, 23, 461.
- (6) Zidan, R. A.; Takara, S.; Hee, A. G.; Jensen, C. M. *J. Alloys Compd.* **1999**, 285, 119.
- (7) Bogdanovic, B.; Brand, R. A.; Marjanovic, A.; Schwickardi, M.; Tölle, J. *J. Alloys Compd.* **2000**, 302, 36–58.
- (8) Gross, K. J.; Guthrie, S.; Takara, S.; Thomas, G. *J. Alloys Compd.* **2000**, 297, 270.
- (9) Zaluska, A.; Zaluski, L.; Ström-Olsen, J. O. *J. Alloys Compd.* **2000**, 298, 125.
- (10) Balema, V. P.; Dennis, K. W.; Pecharsky, V. K. *Chem. Commun.* **2000**, 1665.
- (11) Jensen, C. M.; Gross, K. *J. Appl. Phys. A* **2001**, 72, 213.
- (12) Bogdanovic, B.; Schwickardi, M. *J. Appl. Phys. A* **2001**, 72, 221.
- (13) Chen, J.; Kuriyama, N.; Xu, Q.; Takeshita, H. T.; Sakai, T. *J. Phys. Chem. B* **2001**, 105, 11214.
- (14) Jensen, C. M.; Zidan, R. A. U.S. Patent 6,471,935, 2002.
- (15) Gross, K. J.; Thomas, G. T.; Jensen, C. M. *J. Alloys Compd.* **2002**, 330–332, 691.
- (16) Gross, K.; Sandrock, G.; Thomas, G.; Jensen, C.; Meeker, D.; Takara, S. *J. Alloys Compd.* **2002**, 330–332, 696.
- (17) Thomas, G. J.; Gross, K.; Yang, N. Y. C.; Jensen, C. M. *J. Alloys Compd.* **2002**, 330–332, 702.
- (18) Sun, D.; Kiyobayashi, T.; Takeshita, H. T.; Kuriyama, N.; Jensen, C. M. *J. Alloys Compd.* **2002**, 337, L8.
- (19) Meisner, G. P.; Tibbetts, G. G.; Pinkerton, F. E.; Olk, C. H.; Balogh, M. P. *J. Alloys Compd.* **2002**, 337, 254.
- (20) Sandrock, G.; Gross, K.; Thomas, G. *J. Alloys Compd.* **2002**, 339, 299.
- (21) Fichtner, M.; Fuhr, O. *J. Alloys Compd.* **2002**, 345, 286.
- (22) Bogdanovic, B.; Sandrock, G. *MRS Bull.* **2002**, 27, 712.
- (23) Balogh, M. P.; Tibbetts, G. G.; Pinkerton, F. E.; Meisner, G. P.; Olk, C. H. *J. Alloys Compd.* **2003**, 350, 136.
- (24) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941; p 11.
- (25) Ashby, E. C.; Kobertz, P. *Inorg. Chem.* **1966**, 5, 1615.
- (26) Young, D. A. *The International Encyclopedia of Physical Chemistry and Chemical Physics Topic 21: Solid and Surface Kinetics Vol 1: Dehydrogenation of Solids*; Pergamon Press: Oxford, 1966.
- (27) Borg, R. J.; Dienes, G. J. *The Physical Chemistry of Solids*; Academic Press: San Diego, 1992; p 466.