Kinetics of Aluminum Hydride Thermal Decomposition

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Abstract—The kinetics of AlH_3 decomposition were studied as a function of temperature and hydrogen pressure. Analysis of the experimental data in the formal heterogeneous kinetic approach suggests that the rate of the process is limited by the breaking of Al-H bonds.

INTRODUCTION

Aluminum hydride is of practical and theoretical interest as a hydrogen source and a convenient model system for investigating the thermal decomposition of solids.

Above 160°C, aluminum hydride decomposes rapidly by the reaction AlH₃ \longrightarrow Al + $\frac{3}{2}$ H₂. The thermodynamic characteristics of AlH₃ ($\Delta_f H^0(298.15 \text{ K}) =$ -11.4 kJ/mol, S⁰(298.15 K) = 30.04 J/(mol K), $\Delta_f G^0(298.15 \text{ K}) = 46 \text{ kJ/mol}$) can be used to evaluate the equilibrium hydrogen pressure: $p_{H_2} = 2.6 \times 10^{10} \text{ Pa}$ [1, 2]. The high equilibrium pressure indicates that the process in question is essentially irreversible.

The initial stages of AlH_3 thermal decomposition and the kinetics of later stages, in particular, those stimulated by UV irradiation were studied in [3–5]. Despite the large number of reports concerned with the thermal decomposition of aluminum hydride, the mechanism of this process is still poorly understood and the nature of the rate-limiting step is not yet clear.

The purpose of this work was to clarify the mechanism of AlH_3 decomposition based on experimental kinetic data.

EXPERIMENTAL

We studied samples of polycrystalline aluminum hydride which were stored in air for 10-12 years. The content of AlH₃ was 96% on hydrogen basis.

The samples were placed in a quartz beaker, which was then mounted in an autoclave connected to a gauge or gas burette for pressure or hydrogen-volume measurements. Prior to experiments, the system was evacuated. Then, the autoclave was mounted in a massive metallic rest placed in temperature-controlled electric furnace. The fraction of AlH₃ decomposed at constant pressure and temperature was determined as $\alpha = V/V_{\infty}$ [6], where V is the volume of hydrogen evolved by the instant under consideration and V_{∞} is the volume of hydrogen released as a result of the decomposition of the entire sample. The fraction of the hydride decomposed at constant temperature and volume was calculated as $\alpha = p/p_{\infty}$, where p_{∞} is the maximum pressure in the system, corresponding to full decomposition.

RESULTS AND DISCUSSION

Figures 1 and 2 display a set of kinetic curves describing AlH_3 decomposition at constant temperature and constant or variable (0–1.5 MPa) pressure.

The curves show a well-defined induction period, a sharp rise in the decomposition rate, a period during which the bulk of the sample (80–85%) decomposes, and the final stage.



Fig. 1. Variation of hydrogen volume with time during AlH₃ decomposition at constant pressure and temperature; T = (1) 437, (2) 443, (3) 448, (4) 458 K.

The kinetics of AlH₃ decomposition at an elevated hydrogen pressure were represented by an almost straight line, indicative of a stationary process (Fig. 3). The curves of AlH₃ decomposition at constant volume and 433–448 K showed an inflection, pointing to a stepwise hydrogen release, presumably due to the formation of an intermediate product. At higher temperatures, the inflection was less pronounced.

Since AlH₃ decomposition yields metallic Al, it can be expected that nucleation and growth of aluminum crystals may have a significant effect on the decomposition rate. Then, Al additions to AlH₃ would increase the number of decomposition centers, thereby altering the kinetics of the process. By contrast, gallium might be expected to inhibit the reaction because of the high Al solubility in Ga.

The kinetic curves of AlH_3 decomposition in the presence of Al and Ga are shown in Fig. 2. The effect of Al and Ga on the decomposition rate is seen to be insignificant.

In those experiments, we used Al powder with an oxidized surface layer, probably without nucleation sites. It was, therefore, of interest to carry out decomposition with a halt at an AlH₃ conversion of 15-17%. The crystallites formed in the initial stages were expected to act as seeds during further decomposition. However, in contrast to what was expected, we observed a reduction in the rate of AlH₃ decomposition (Fig. 2).

Curves 1-3 in Fig. 2 were obtained at an initial hydrogen pressure of 1.08 MPa. Increasing the hydrogen pressure to just above the equilibrium value $p_{\rm H_2} = 2.6 \times 10^{10}$ Pa notably changes the kinetics of the process: the decomposition rate first gradually rises and then decreases.

Similar results were obtained when the samples were preliminarily held at ≤433 K in vacuum for 20 min.

Therefore, it seems likely that the reduced decomposition rate at an elevated hydrogen pressure or after holding at an elevated temperature is associated with a decrease in the amount of nucleation sites and an increase in the activation energy of nucleation.

Subsequently, nucleation proceeds at a constant rate, according to the first-order rate law, $d\alpha/d\tau = kN$ (where N is the number of potential nucleation sites at time τ), and a steady state is reached.

In fitting kinetic data and calculating process parameters, we used different equations of heterogeneous kinetics (Table 1) [7–9].

Generally, the rate of AlH₃ decomposition can be represented by a function of separable variables, $d\alpha/d\tau = \omega f(\alpha)$, where ω is the temperature- and pressure-dependent reaction rate, and $f(\alpha)$ characterizes the change in the reaction surface area in unit time.

Fitting the experimental data with the kinetic equations given in Table 1, we obtained almost straight lines Fig. 2. Variation of hydrogen pressure with time during AlH₃ decomposition at constant volume and temperature: (1) 435 K; (2) 477 K, (3) 495 K; (4) 465 K, elevated hydrogen pressure; (5) 458 K, with a halt; (6) 458 K, after holding at 403–433 K; (7) 458 K, in the presence of Al or Ga.



Fig. 3. Conversion vs. time for AlH₃ decomposition at constant volume and temperature; T = (1) 495, (2) 477, (3) 459, (4) 433 K.

on α -vs.- $\tau/\tau_{0.5}$ plots, where $\tau_{0.5}$ is the time taken for half of the sample to decompose. At the same time, such plots allow one to exclude the effects of temperature and pressure because the mechanism of AlH₃ decomposition does not change with time—the sequence of reaction steps remains the same.

Isothermal AlH₃ decomposition can be fitted to the Hill equation in differential form,

$$d\alpha/d\tau = \omega(1-\alpha)[A^2 + \ln^2(1-\alpha)]^{1/2}, \qquad (1)$$

or integral form,

$$-\ln(1-\alpha) = A\sinh(\omega\tau).$$
(2)

The calculated rate parameters are listed in Tables 2 and 3. The activation energies of AlH_3 decomposition

Equation	Analytical form
(1) Nucleation	
Prout–Tompkins	$\ln[\alpha/(1-\alpha)] = \omega \tau + \text{const}$
Avrami–Erofeev	$-\ln(1-\alpha) = (\omega\tau)^n$
Hill	$-\ln(1-\alpha) = A\sinh(\omega\tau)$
(2) Growth	
first order in surface area	$\ln(1-\alpha) = \omega \tau$
second order	$(1-\alpha)^{-1} = \omega \tau$
contracting sphere	$1 - (1 - \alpha)^{1/3} = \omega \tau / R_0$
contracting surface	$1 - (1 - \alpha)^{1/2} = \omega \tau / R_0$
(3) Diffusion	
one-dimensional	$\alpha^2 = \omega \tau$
two-dimensional	$\alpha + (1 - \alpha) \ln(1 - \alpha) = \omega \tau$
three-dimensional	$[1 - (1 - \alpha)^{1/3}]^2 = \omega \tau$
(4) Gistling–Braunstein	$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=\omega\tau$

or

Table 1. Equations used to fit kinetic data on AlH₃ decomposition

at constant volume and pressure are 37 and 32 kJ/mol, respectively (Fig. 4).

decomposition rate at this stage depends on the hydrogen pressure. The corresponding quasi-chemical reaction has the form

 $Al_{A1}^{\times} + H_{H}^{\times} = Al_{A1}' + V_{H}' + \frac{1}{2}H_{2}$

MECHANISM OF AIH₃ DECOMPOSITION

The inhibiting effect of hydrogen pressure on the thermal decomposition of AlH_3 can be understood under the assumption that the process involves the following stages:

$$AlH_{3-x} \xrightarrow{K_1} AlH_{1-x} + H_2,$$
 (3)

$$AIH_{1-x} \to AI + \frac{1}{2}H_2.$$
 (4)

The former stage is rapid and reversible. The



Fig. 4. Logarithm of the decomposition rate vs. inverse temperature: (1) constant volume; (2) constant pressure.

$$AI_{AI}^{*} + 2H_{H}^{*} = AI_{AI}^{"} + 2V_{H}^{*} + H_{2},$$

where AI_{A1}^{\times} and H_{H}^{\times} are, respectively, aluminum and hydrogen atoms on normal lattice sites; AI_{A1}^{\prime} and AI_{A1}^{\prime} are aluminum ions in the oxidation states 2+ and 1+, respectively; and V_{H}^{\cdot} is a positively charged hydrogen vacancy. These reaction schemes assume that molecular hydrogen, having a lower reducing ability, is released during AlH₃ decomposition, instead of atomic hydrogen.

The expression for the decomposition rate can be obtained by assuming a particular reaction mechanism and using equations (3) and (4). The general expression for the decomposition rate has the form

$$d[AlH_{3-x}]/d\tau = -K_1[AlH_{3-x}] + K_2[AlH_{1-x}][H_2].$$
(5)

Using the Bodenstein-Semenov constant-concentration method [10-13], we obtain

$$d[AlH_{1-x}]/d\tau = K_1[AlH_{3-x}] - K_2[AlH_{1-x}][H_2] - K_3[AlH_{1-x}] \approx 0.$$
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Table 2. Rate of AlH₃ decomposition as a function of temperature at p = const; A = 0.01, $E_a = 37$ kJ/mol

<i>T</i> , K	437	443	448	458
τ _{0.5} , s	327	264	245	218
$\omega \times 10^3$, s ⁻¹	15.08	18.67	22.62	20.12

Table 3. Rate of AlH₃ decomposition as a function of temperature at V = const; A = 0.2, $E_a = 32$ kJ/mol

<i>T</i> , K	435	459	474	495
τ _{0.5} , s	335	200	147	92
$\omega \times 10^3$, s ⁻¹	5.85	9.8	13.33	21.3

Therefore,

$$[A|H_{1-x}] = K_1[A|H_{3-x}]/(K_2[H_2] + K_3),$$

since

$$d[\mathrm{AlH}_{1-x}]/d\tau = 0.$$

Substituting $[AlH_{1-x}]$ in (5), we find

$$\frac{d[\text{AlH}_{3-x}]}{d\tau} = -\frac{K_1[\text{AlH}_{3-x}] + K_2K_1[\text{AlH}_{3-x}]}{K_3 + K_2[\text{H}_2]}$$
$$= -\frac{K_3[\text{AlH}_{3-x}]}{(K_2/K_1[\text{H}_2] + K_3/K_1)}.$$

Taking $\omega_{\text{max}} = -K_3 \text{AlH}_{3-x}$, we have

$$\omega = \omega_{\max} K_1 / (K_2[H_2] + K_3)$$

or

$$1/\omega = K_2[H_2]/K_1\omega_{\max} + K_3/K_1\omega_{\max}.$$
 (6)

It follows from (6) that $1/\omega$ is linear in H₂, in accordance with the observed effect of hydrogen pressure on the rate of AlH₃ decomposition.

The proposed mechanism suggests that the rate of the process is limited by the breaking of bonds in the $[A|H_{1-x}]$ complex, rather than by the formation of active centers (Al⁰).

CONCLUSION

The kinetics of AlH_3 decomposition were studied at different temperatures, and the kinetic parameters of the process were determined. Increasing the hydrogen pressure or preheating the sample was found to reduce the decomposition rate. The decomposition kinetics are best fitted with the Avrami–Erofeev and Hill equations, suggesting a branched-chain mechanism. Based on the kinetic data, we can conclude that the rate of the process is limited by the breaking of Al–H bonds, rather than by the formation of Al nucleation sites.

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