Catalytic Action of Atmospheric Water Vapor on the Thermal Decomposition of Synthetic Hydrozincite

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The effect of atmospheric water vapor on the kinetic rate behavior of the thermal decomposition of zinc carbonate hydroxide, Zn₅(CO₃)₂(OH)₆, was investigated by means of TG-DTA under the controlled partial pressure of atmospheric water vapor, p(H₂O). With increasing p(H₂O) from 0.7 to 9.4 kPa, the reaction temperature at the restricted heating rate was reduced systematically accompanied by the change in the shape of TG curves. Through systematic kinetic analysis of the reaction at different p(H₂O), the change in the kinetic behavior was characterized by the mutually dependent decreases in the apparent activation energy and the Arrhenius pre-exponential factor, where the catalytic action of atmospheric water vapor on the surface nucleation process was identified as the possible mechanistic origin.

Key words: Hydrozincite, Kinetics, Thermal Decomposition, Water Vapor Pressure, Zn₅(CO₃)₂(OH)₆

1. INTRODUCTION

The concentration of product gas in the reaction atmosphere is one of the important factors affecting on the kinetic behavior of the thermal decomposition of inorganic solids. From a simple view point of chemical equilibrium, the reaction rate is decelerated with increasing the concentration of product gas. Exceptionally, several examples of catalytic action of the product gas had been found for the thermal dehydration of inorganic hydrates, known as Smith-Topley behavior [1]. For more complicated cases which evolves more than one kind of product gases in a single decomposition step, different effects of the respective product gases on the kinetic behavior is also expected. Recently, we encountered such complicated effects of the product gases for the thermal decompositions of some basic carbonates of transition metals [2-5] and sodium hydrogencarbonate [6], where the respective effects of two product gases, CO₂ and H₂O, on the kinetic behavior were characterized as the normal effect in view of chemical equilibrium and catalytic effect in view of reaction kinetics, respectively.

In the present study, the thermal decomposition of zinc carbonate hydroxide (ZCH), Zn₅(CO₃)₂(OH)₆, corresponding to the mineral hydrozincite [7], was subjected to the kinetic study for examining the catalytic action of the water vapor on the kinetic behavior. For the present reaction which evolves CO₂ and H₂O simultaneously by producing ZnO, the catalytic action of self-generated water vapor has been confirmed in our previous study using Controlled Rate Evolved Gas Analysis (CREGA) coupled with TG [4]. By applying TG-DTA coupled with a programmable humidity controller, the rate behavior of the thermal decomposition in the higher p(H₂O) region was investigated in the present study. Through systematic kinetic analysis for the reaction processes at various p(H₂O), the possible origin of the catalytic action was interpreted from the view point of overall kinetics.

2. EXPERIMENTAL

The same batch of ZCH prepared and identified in our previous study [4,7] was utilized after confirming by powder X-ray diffractometry, FT-IR spectroscopy and TG-DTA that there is no degeneration by ageing.

By keeping the samples of ca. 10.0 mg at 350 K in an instrument of TG-DTA (Rigaku TG8120), a mixed gas of N₂-H₂O with a controlled p(H₂O) was introduced into the reaction tube at a rate of ca. 450 cm³ min⁻¹ from a programmable humidity controller (Rigaku HUM-1). After stabilizing the reaction system for 30 min, the sample was heated at various heating rates β for recording TG-DTA.

3. RESULTS AND DISCUSSION

3.1 Effect of p(H₂O) on reaction temperature

Figure 1 compares TG-derivative TG (DTG) curves (β=5 K min⁻¹) for the thermal decomposition of ZCH at various controlled p(H₂O). Although the thermal decomposition process is a well-defined single mass-loss step irrespective of p(H₂O) applied, the reaction temperature shifts to the lower temperature region with increasing p(H₂O). This behavior is in accordance with that observed previously in the lower p(H₂O) by CREGA-TG [4], indicating the apparently opposite trend from a view point of chemical equilibrium: Zn₅(CO₃)₂(OH)₆ ⇌ 5ZnO + 2CO₂ + 3H₂O. The reduction of reaction temperature with p(H₂O) was reproduced by following the changes of the extrapolated onset temperature, Tₑ.o., and peak top temperature, Tₑ, of the DTG curves as shown in Fig. 2. By increasing p(H₂O) from 0.7 to 9.4 kPa, Tₑ.o. and Tₑ have decreased...
continuously by 27.6 and 17.9 K, respectively. From the difference in the change of $T_{e.o.}$ and $T_p$, it is expected that the variation of the kinetic behavior observed results from an interdependent change in the values of apparent activation energy, $E_a$, and the Arrhenius pre-exponential factor, $A$, accompanied possibly by the gradual change in the physico-geometric mechanism of the reaction.

3.2 Effect of $p$(H$_2$O) on apparent activation energy

By selecting four different controlled $p$(H$_2$O), i.e., 0.7, 1.0, 3.6, and 6.1 kPa, TG measurements at various $\beta$ were carried out for recording the series of kinetic rate data. Figure 3 shows the series of TG-DTG curves for the thermal decomposition at $p$(H$_2$O)=6.1 kPa. Irrespective of the controlled $p$(H$_2$O) applied, the kinetic rate data shift systematically to the higher temperature with increasing $\beta$.

For the kinetic analysis, the following kinetic equation was assumed:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (1),$$

where $\alpha$ and $f(\alpha)$ are the fractional reaction and kinetic model function, respectively. According to the Friedman method [8], the values of $E_a$ at various $\alpha$ were evaluated by applying the logarithmic form of eq.(1) to the data points at selected $\alpha$ of the series of kinetic rate data at various $\beta$. Figure 4 shows typical plots of $\ln(d\alpha/dt)$ against $T^{-1}$ at various $\alpha$ for the kinetic rate data at $p$(H$_2$O)=6.1 kPa. The Friedman plots indicate linear correlations irrespective of $\alpha$, where the slopes of the plots at different $\alpha$ are nearly constant. The similar results of the Friedman plots were observed also for the kinetic rate data at $p$(H$_2$O) of 0.7, 1.0 and 3.6 kPa.

The values of $E_a$ at various $\alpha$ for the reactions at different $p$(H$_2$O) are compared in Fig. 5. Although the values of $E_a$ are nearly constant except the initial and final parts of the reaction, it is apparent that the values of $E_a$ decreases slightly but systematically with increasing $p$(H$_2$O). Table I lists the averaged values of $E_a$ (0.1 $\leq \alpha \leq$ 0.9) at different $p$(H$_2$O).

3.3 Effect of $p$(H$_2$O) on apparent rate behavior

For evaluating the effect of $p$(H$_2$O) on the apparent rate behavior, the experimental master plots were drawn by extrapolated the kinetic rate data to infinite temperature according to the isocconversional relationship [9,10]:
p(H₂O) is attenuating with increasing decelerate part observed for the reaction at the lower experimental master plots, i.e., \( d_\theta = \frac{d_\alpha}{E_p} \exp \left( \frac{E_p}{RT} \right) \)

with \( \theta = \int_0^\alpha \exp \left( -\frac{E_p}{RT} \right) \, dt \quad (2) \),

where \( \theta \) is the Ozawa’s generalized time \([11]\) denoting the reaction time at infinite temperature. The experimental master plots, i.e., \( d_\alpha/d\theta \) vs. \( \alpha \) \([12]\), drawn by adopting the values of \( E_p \) listed in Table I are compared in Fig. 6. Although the established part of reaction (0.25 ≤ \( \alpha \) ≤ 0.9) indicates the maximum rate at around \( \alpha \approx 0.4 \) irrespective of \( p(H₂O) \), the initial decelerate part observed for the reaction at the lower \( p(H₂O) \) is attenuating with increasing \( p(H₂O) \).

By combining eqs. (1) and (2), \( d_\alpha/d\theta \) can be correlated to \( A \) and \( f(\alpha) \) as follows \([9,10]\):

\[
\frac{d_\alpha}{d\theta} = A f(\alpha) \quad (3).
\]

Because the present reaction is characterized by the initial decelerate process observed for the reactions at the lower \( p(H₂O) \) and the established part of the reaction with the maximum reaction rate, the respective parts of the reaction were correlated separately to possible \( f(\alpha) \) by evaluating the kinetic exponents and the value of \( A \) simultaneously through the nonlinear least square fitting by the Levenberg-Marquardt optimization algorithm \([13,14]\).

For fitting the experimental master plots of the initial decelerate process (0.10 ≤ \( \alpha \) ≤ 0.20), several physico-geometric \( f(\alpha) \) which describes diffusion controlled interface movement with different reaction geometries were applied. As the results, a diffusion controlled nucleus growth model known as Johnson-Mehl-Avrami equation, JMA(\( m \)) with 0.5 ≤ \( m \) < 1 \([1]\), was selected as the most appropriate \( f(\alpha) \):

\[
f(\alpha) = m(1-\alpha)^{\frac{1}{1-m}} \quad (4).
\]

Fig. 6 shows the fitting curve of JMA(\( m \)) with \( m = 0.68 \) for the initial decelerate part of the reaction at \( p(H₂O) = 0.7 \) kPa.

For the first sake of apparent curve fitting, an empirical kinetic model function known as Sestak-Berggren model with three kinetic exponents, SB(\( m, n, p \)) \([15]\), was applied to the established part of the reaction (0.25 ≤ \( \alpha \) ≤ 0.90):

\[
f(\alpha) = \alpha^m (1-\alpha)^n \left[ -\ln(1-\alpha) \right]^{1-p} \quad (5).
\]

The fitting curves of SB(\( m, n, p \)) for the established part of reactions at \( p(H₂O) = 0.7 \) and 6.1 kPa were shown in Fig. 7. The experimental master plots of the established part of reaction are nearly perfectly fitted, but the physico-chemical significance of the sets of kinetic exponents are not clear as the compensation for the high flexibility of the empirical model \([16]\).

### Table I  Kinetic parameters evaluated for the thermal decomposition of ZCH at different \( p(H₂O) \)

<table>
<thead>
<tr>
<th>( p(H₂O) / \text{kPa} )</th>
<th>( E_p^* / \text{kJ mol}^{-1} )</th>
<th>Range of ( \alpha )</th>
<th>( f(\alpha) )</th>
<th>( A / \text{s}^{-1} )</th>
<th>( \gamma^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>117±5</td>
<td>0.10 ≤ ( \alpha ) ≤ 0.20</td>
<td>JMA(0.68)</td>
<td>(4.16±0.14)×10^7</td>
<td>0.9837</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25 ≤ ( \alpha ) ≤ 0.90</td>
<td>SB(-3.16, 2.76, 3.91)</td>
<td>(1.83±0.08)×10^4</td>
<td>0.9992</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>JMA(1.76)</td>
<td>(7.29±0.18)×10^6</td>
<td>0.9485</td>
</tr>
<tr>
<td>1.0</td>
<td>114±3</td>
<td>0.10 ≤ ( \alpha ) ≤ 0.20</td>
<td>JMA(0.73)</td>
<td>(2.31±0.04)×10^6</td>
<td>0.9933</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25 ≤ ( \alpha ) ≤ 0.90</td>
<td>SB(-3.91, 2.92, 4.52)</td>
<td>(7.30±0.31)×10^7</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>JMA(1.72)</td>
<td>(3.58±0.07)×10^5</td>
<td>0.9618</td>
</tr>
<tr>
<td>3.6</td>
<td>94±2</td>
<td>0.25 ≤ ( \alpha ) ≤ 0.90</td>
<td>SB(-4.57, 2.93, 5.01)</td>
<td>(6.18±0.28)×10^6</td>
<td>0.9986</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>JMA(1.83)</td>
<td>(3.89±0.06)×10^7</td>
<td>0.9799</td>
</tr>
<tr>
<td>6.1</td>
<td>92±1</td>
<td>0.25 ≤ ( \alpha ) ≤ 0.90</td>
<td>SB(-2.23, 1.87, 2.66)</td>
<td>(5.16±0.15)×10^5</td>
<td>0.9993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>JMA(1.91)</td>
<td>(3.09±0.02)×10^8</td>
<td>0.9968</td>
</tr>
</tbody>
</table>

* Averaged over 0.10 ≤ \( \alpha \) ≤ 0.90.
The JMA(m) of nucleation and growth type model was also applied for evaluating the physico-chemical mechanisms of the established reaction. The experimental master plots were fitted by the JMA(m) with m slightly smaller than 2. The accuracy of the fitting by JMA(m) is improved with increasing p(H2O), indicating the acceptable fitting comparable with SB(m,n,p) at the higher p(H2O), see Fig.7(b). The behavior is due to the gradual disappearance of initial decelerate process of surface reaction with increasing p(H2O). The agreement of the established reaction to JMA(m) with n=2 is in accordance with the previous results evaluated for the present reaction at the lower p(H2O) using CREGA-TG [4].

3.4 Kinetic interpretation
The kinetic results evaluated in the present study were summarized in Table I. At the lower p(H2O), the reaction is described by the partially overlapped processes of initial decelerate process of surface reaction characterized by JMA(m) with 0.5≤m<1 and the established reaction controlled by nucleation and growth mechanism, i.e., JMA(m) with m=2. The disappearance of the initial decelerate process with increasing p(H2O) promotes the reduction of the reaction temperature, indicating the catalytic action of atmospheric water vapor on the surface nucleation process. The catalytic action of water vapor on the surface reaction has also been observed for the thermal decomposition of copper(II) carbonate hydroxide [5] and is one of the most possible causes of the Smith-Topley effect [1].

From the viewpoint of overall kinetics, the catalytic action is evaluated by the decrease in the value of Ea

from 117 to 92 kJ mol⁻¹ with increasing p(H2O) from 0.7 to 6.1 kPa, accompanied by the interdependent decrease in the value of A [17] from the order of ~10¹⁵ to ~10⁷ s⁻¹. Due to the kinetic compensation effect of the mutual dependence of Ea and A, the reduction of the reaction temperature by the effect of atmospheric water vapor is estimated as smaller than that expected from the decrease in the value of Ea.

4. CONCLUSIONS
The enhancement of reactivity for the thermal decomposition of ZCH by atmospheric water vapor was evidenced experimentally within increasing p(H2O) from 0.7 to 9.4 kPa. The apparent rate behavior of reducing the thermal stability by the atmospheric water vapor was characterized by the decrease in the value of Ea compensated partially by the parallel decrease in the value of A. From a physico-geometric view point of reaction mechanism, the decelerate process of surface reaction observed at the lower p(H2O) during the initial part of the reaction was gradually attenuated with increasing p(H2O). As the result, at the higher p(H2O) the established reaction controlled by JMA(m) with m=2 was to be dominant during the whole course of reaction. The change in the reaction mechanism indicates that the reduction of reaction temperature is due to a catalytic action of atmospheric water vapor to the surface reaction of the thermal decomposition.

5. REFERENCES