2P27　　　　Impact of atmospheric water vapor on the kinetics of the induction period of the thermal dehydration of lithium sulfate monohydrate

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The thermal dehydration of lithium sulfate monohydrate (LSM) exbibits significant induction period (IP) prior to mass-loss process under isothermal conditions. The average rate of IP is well described by conventional Arrhenius-type temperature dependence. The kinetic behavior of IP dramatically changes by the influence of the atmospheric water vapor pressure, $p(H_2O)$. In this study, a universal kinetic description for the induction period under various temperature, T, and $p(H_2O)$ was trialed through formalizing an accommodation function, $a(p(H_2O), P_{eq}(T))$, on the basis of classical nucleation theory. Characteristic kinetic behavior of the IP process is discussed by reviewing the results of the universal kinetic approach.

Figure 1 shows the variation in IP duration, t_{IP}, depending on T and $p(H_2O)$. The t_{IP} value increases exponentially with deceasing T under selected $p(H_2O)$ value. At a selected T, t_{IP} value increases with increasing $p(H_2O)$ value. The following kinetic equation that consider the dependence of average rate of IP on T and $p(H_2O)$ was assumed.

$$\frac{1}{t_{IP}} = A_{IP}\exp\left(-\frac{E_{a,IP}}{RT}\right)f(\alpha_{IP})a\bigl(p(H_2O),P_{eq}(T)\bigr) \qquad (1)$$

Where A_{IP}, $E_{a,IP}$ and $f(\alpha_{IP})$ are the apparent preexponential factor, activation energy, and kinetic model function, respectively. For $a(p(H_2O), P_{eq}(T))$, the following function was derived from the classical nucleation theory.

$$a\bigl(p(H_2O),P_{eq}(T)\bigr)=\left(\frac{P_0}{p(H_2O)}\right)^a\left[1-\left(\frac{p(H_2O)}{P_{eq}(T)}\right)^b\right] \qquad (2)$$

where $P_{eq}(T)$ and P_0 are the equilibrium and atmospheric pressures, respectively. On the basis of eq. (1), the Arrhenius-type plot was applied to the IP process under various T and $p(H_2O)$ conditions through optimizing the exponents (a, b) in eq. (2) so as to obtain the best linear correlation. Figure 2 shows the Arrhenius-type plot based on eq. (1). Although the plot exhibits statistically significant linear correlation, two temperature regions characterized by different linear correlations were observed, which is separated at approximately 371 K. The change in the kinetic behavior at approximately the boiling point of water indicates the significant contribution of water vapor desorption from the surface on the kinetics of the IP process.
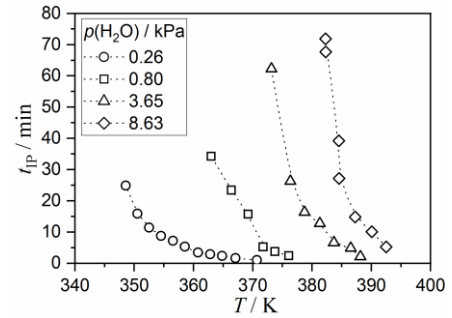

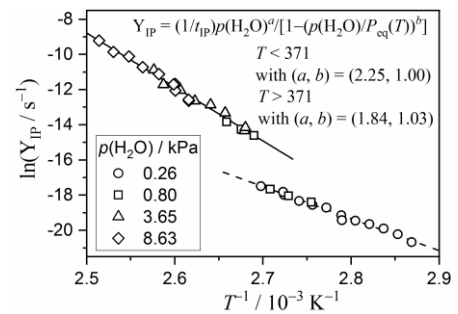Fig.1 IP duration, t_{IP}, at different T and $p(H_2O)$.

Fig.2 Arrhenius-type plots for the IP process at different T and $p(H_2O)$.