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Masahiro Fukuda, Nobuyoshi Koga, Loïc Faveregeon. Kinetics and mechanisms of the thermal decomposition of copper(II) hydroxide under different water vapour pressures. ESTAC12 - The 12th European Symposium on Thermal Analysis and Calorimetry, Central and Eastern European Committee for Thermal Analysis and Calorimetry (CEEC-TAC); Transilvania University of Brasov (UniTBv); National Institute for Laser, Plasma and Radiation Physics (INFLPR); Institute of Physical Chemistry "Ilie G. Murgulescu" of the Romanian Academy (ICF); Commission for Thermal Analysis & Calorimetry of the Romanian Academy (CATCAR), Aug 2018, Brasov, Romania. pp.424 / PS2.058. hal-01898543

HAL Id: hal-01898543

<https://hal.science/hal-01898543v1>

Submitted on 29 Nov 2018

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Kinetics and mechanisms of the thermal decomposition of copper(II) hydroxide under different water vapour pressures

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Thermal decomposition of Cu(OH)₂ exhibits specific physico-geometric kinetic characteristics involving the significant induction period (IP) and subsequent sigmoidal mass-loss behaviour under isothermal conditions and the two-step mass-loss process with a long lasting reaction tail under linearly increasing temperature conditions. In addition, the rate behaviours of IP and mass-loss process are largely influenced by the environmental water vapour pressure, $p(\text{H}_2\text{O})$. The IP at a constant temperature is prolonged with increasing $p(\text{H}_2\text{O})$. The mass-loss curves shift systematically to higher temperatures with increasing $p(\text{H}_2\text{O})$. Therefore, the kinetic approach to this complex reaction requires the detailed considerations of the mechanistic features and the impact of $p(\text{H}_2\text{O})$.

For the universal kinetic approach to each kinetic process under different $p(\text{H}_2\text{O})$, an accommodation function with respect to $p(\text{H}_2\text{O})$ was derived:

$$a(p(\text{H}_2\text{O}), P_{\text{eq}}(T)) = \frac{1}{p(\text{H}_2\text{O})^m} \left[1 - \left(\frac{p(\text{H}_2\text{O})}{P_{\text{eq}}(T)} \right)^n \right]$$

The accommodation function $a(p(\text{H}_2\text{O}), P_{\text{eq}}(T))$ can be introduced into different kinetic equations for describing the IP and mass-loss process. The IP at different temperatures and under different $p(\text{H}_2\text{O})$ analysed kinetically by a single Arrhenius-type plot, providing a statistically significant linearity and the activation energy $E_{a,\text{IP}} = 243 \pm 13 \text{ kJ mol}^{-1}$. Similarly, $a(p(\text{H}_2\text{O}), P_{\text{eq}}(T))$ is introduced into the isoconversional kinetic equation for analyzing universally the mass-loss process under different temperature conditions and $p(\text{H}_2\text{O})$. The isoconversional plots applied to the major mass-loss step of the thermal decomposition of Cu(OH)₂ represent straight lines and the average $E_{a,1} = 148 \pm 1 \text{ kJ mol}^{-1}$ (Fig. 1). Furthermore, the overall thermal decomposition of Cu(OH)₂ under isothermal conditions can be described by the IP–surface reaction (SR)–phase boundary controlled reaction (PBR) model [1]. The rate constants of each component reaction step determined under different $p(\text{H}_2\text{O})$ are subjected to the Arrhenius plot by considering $a(p(\text{H}_2\text{O}), P_{\text{eq}}(T))$.

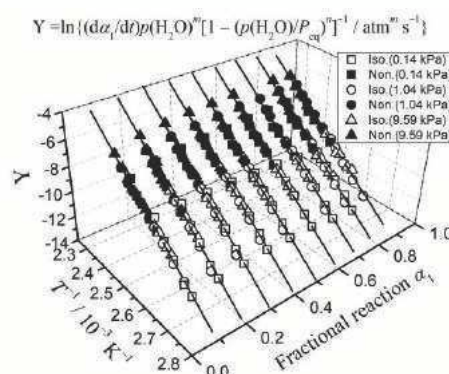


Fig. 1. The results of the universal Friedman plot applied to the first mass-loss step of thermal decomposition of Cu(OH)₂ under different $p(\text{H}_2\text{O})$.

REFERENCE

[1] H. Ogasawara, N. Koga, J. Phys. Chem. A., 118 (2014) 2401