Non-Isothermal Kinetics and Mechanistic Study of Thermal Decomposition of Light Rare Earth Metal Nitrate Hydrates Using Thermogravimetric Analysis

Bamidele V. Ayodele, Mohammed Anwar Hossain, Soo Ling Chong, Jiah Chee Soh, Sureena Abdullah, Maksudur R. Khan, Chin Kui Cheng
Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang

ABSTRACT
The formation of light rare earth metal oxides such as CeO_2, La_2O_3, Sm_2O_3, Nd_2O_3 and Pr_2O_3 from thermal decomposition of its nitrate precursors ($Ce(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$ and $Pr(NO_3)_3{\cdot}6H_2O$) have been investigated by thermogravimetric analysis. The rare earth metal oxides obtained were characterized for the nature of chemical bonds and textural properties using FTIR and N_2-physisorption analyses, respectively. The FTIR analysis of the rare earth metal precursors and the oxides showed that the OH– and NO– bonds depicting the presence of hydrated water molecules and nitrate disappeared after the thermal decomposition leaving out only the pure solid oxides. The kinetics data obtained from the thermogravimetric analysis were fitted into "model free" kinetic expressions such as Kissinger, Ozawa–Flynn–Wall to calculate the apparent activation energy of the solid-state decomposition reaction of the rare earth metal precursors. The kinetic parameters were further analyzed using Coat–Redfern model to determine the possible mechanism of the decomposition process. The calculated values of the activation energy obtained from both Kissinger and Ozawa–Flynn–Wall models were similar compared to that obtained from Coat–Redfern model. Highest activation energies of 230.26, 344.78, 320.2.78, 392.72 and 258.26 kJ mol^{-1} were obtained from decomposition of $Ce(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$ and $Pr(NO_3)_3{\cdot}6H_2O$), respectively, using Kissinger model, while the analysis of the kinetic data using Ozawa–Flynn–Wall model gave the highest activation energies of 229.01, 350.56, 348.56, 392.72 and 388.56 kJ mol^{-1} for decomposition of $Ce(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$ and $Pr(NO_3)_3{\cdot}6H_2O$), respectively. Thirteen different models were evaluated using Coat–Redfern models in order to determine the mechanisms that govern the decomposition process. Interestingly, two-dimensional diffusion mechanism with activation energy of 105.61, 107.61, 140.61, 144.52 and 154.78 kJ mol^{-1} was obtained for thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$ and $Pr(NO_3)_3{\cdot}6H_2O$), respectively. The rare earth metal oxides obtained from this study finds potential application as supports, promoters and catalysts in the field of catalysis.

KEYWORDS: Kinetics; Thermogravimetry analysis; Rare earth metals; Thermal decomposition; Solid-state reaction

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