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The non-isothermal kinetics of hydroxyapatite formation in kaolin - natural phosphate mixtures

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Abstract

In this work, the activation energy of hydroxyapatite formation in different composites under non-isothermal conditions was determined using differential thermal analysis (DTA). Seven compositions were prepared and studied while varying the percentage of the kaolin from 20 to 80 wt.% at 10% increments. The DTA conducted at heating rates of 10, 20 and 30 K min^{-1} showed an exothermic peak in all composites in the region 700°C–750°C associated with hydroxyapatite formation. The activation energies measured from non-isothermal treatments for seven compositions (20, 30, 40, 50, 60, 70 and 80 mass% of kaolin) were 194, 178, 178, 209, 162, 146 and 121 kJ mol^{-1}, respectively.

Keywords: non-isotherma, kinetics, hydroxyapatite, kaolin - natural

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1. Introduction

Hydroxyapatite, HAp, is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$ but is usually written $Ca_{10}(PO_4)_6(OH)_2$ with the Ca/P ratio being 1.67. Hap is the hydroxyl end member of the complex apatite group (Elashmawi, Abdelrazek & Aly, 2015).

As a bioceramic material, ceramic hydroxyapatites are widely employed in various biomedical applications, which involve the exploitation of their excellent biocompatibility and surface-active properties with living tissue (Yeong, Wang & Ng, 2001).

The sintering of Algerian kaolin nuances known as (DD1, DD2 and DD3) from Djebel Debbagh has been studied by some researchers. Natural phosphate (NP) is a general term that describes naturally occurring mineral assemblages containing a high concentration of phosphate minerals. About 80 wt% of world NP production is derived from deposits of sedimentary marine origin mainly composed of apatite's (Chouia, Belhouchet, Sahnoune & Bouzrara, 2015). Reaction sintering of kaolin and NP is an easy and inexpensive route to obtain homogenous composites (anorthite–HAp- β-TCP, anorthite–HAp, Hap–anorthite, anorthite and anorthite–mullite) (Belhouchet, Chouia, Hamidouche & Leriche, 2016).

Differential thermal analysis (DTA) has been extensively employed as a rapid and convenient instrument for the study of the kinetics of phase transformation processes and chemical reaction mechanisms. This method was also used to investigate crystallisation kinetics in ceramics, to determine homogeneous crystal nucleation rates and to obtain the activation energy for new phase crystallisation (Belhouchet, Hamidouche, Torrecillas & Fantozzi, 2014).

The objective of this work is to study the effect of kaolin addition on sintering kinetics and reaction between NP and kaolin. The kinetics of hydroxyapatite crystallisation were determined and discussed.

2. Materials and experimental procedures

In our experimental studies, the following powders were used as starting materials:

- Kaolin (DD2) from Djebel Dbag in Guelma. Its chemical composition in mass% is SiO_2(45.52), Al_2O_3(38.75), CaO(0.18), Fe_2O_3(0.096), Na_2O(0.34), K_2O(0.03) and L.O.I(15,44).
- NP from the mine of Djebel Onk (East of Algeria). Its chemical composition in mass% is SiO_2(02.30), Al_2O_3(0.41), CaO(53.16, P_2O_5(26.74), Fe_2O_3(0.69), Na_2O (0.85), SO_3(3.26), K_2O(0.10), MgO(0.75) and L.O.I (11,74).

Cylindrical specimens with a diameter of 13 mm and different thicknesses ranged from 5 to 6 mm were produced. The pressed compacts were heated up to 800°C at a rate of 10 K min^{-1} to avoid cracking the samples. In order to determine an optimum preliminary sintering temperature, the compacts were sintered under atmospheric conditions at different temperatures within the range of 1,000°C–1,400°C with a step of 50°C for 2 hours of soaking and cooled down inside the furnace. The heating rate was kept constant and equal to 10°C min^{-1}.

Powders were subjected to DTA and thermogravimetric analysis (TG) using Setaram Setsys 16/18 simultaneous TG/DTA analyzer with alumina as the reference material. About 40 mg of powders mixture was placed in alumina crucibles and heated at a rate of 10°C min^{-1} from room temperature to 1,300°C. XRD analyses were carried out using a Bruker D8 diffractometer. The XRD test conditions were Ni-filtered Cuk a X-radiation (35 kV–30 mA) with a scanning speed of 37° (2 hours) per minute and at an increment of 0.05°. The morphology of the samples was observed by scanning electronic microscopy (Hitachi S3500-N).

3. Results and discussion

DTA curves for the five compositions (20, 30, 40, 50, 60, 70 and 80 mass% kaolin content) heated at a rate of 10, 20 and 30°C min^{-1} are presented in Figure 1. The shape and area of the third endothermic peak vary with kaolin content.

The DTA curve shows two exothermic peaks. First, one, observed around 732°C, is due to the partial crystallisation of HAp (Bolelli et al., 2014; Koumoulidis et al., 2003), whereas the later observed at 931°C indicate some order in a crystalline formation. Some workers attribute this reaction to spinel formation, while others attribute it to mullite nucleation (Harabi et al., 2014; Ke, Cheng, Wang, Wang & Wang, 2013).

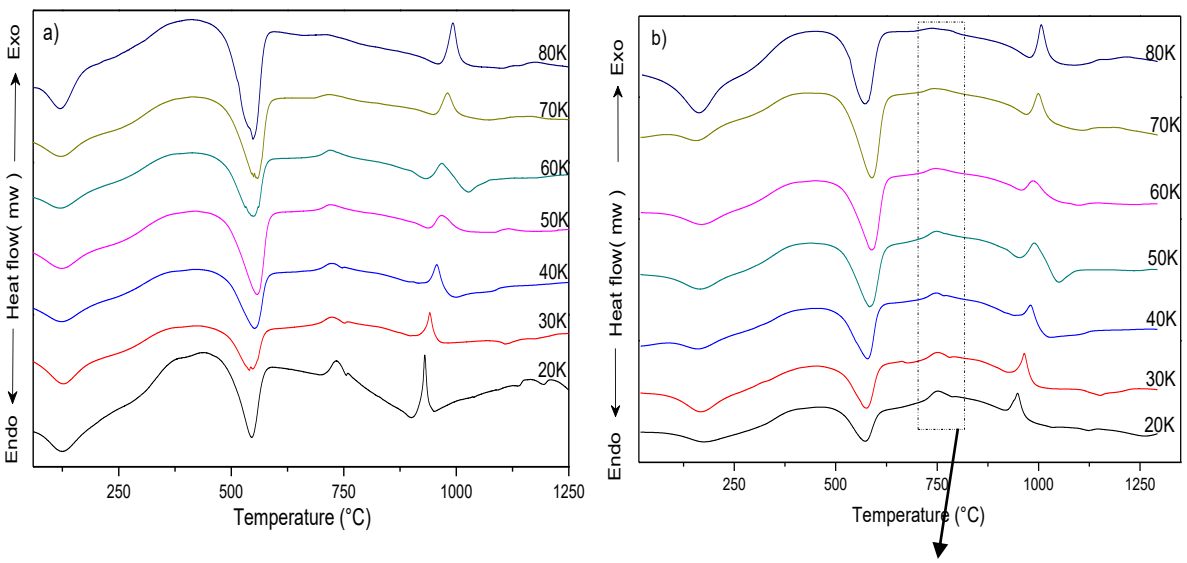
Table1 shows the Tp values of the seven compositions at different heating rates. It can be seen that the temperature of the maximum of this peak position, Tp, decreases from 732.3°C to 714°C with increasing kaolin content from 20 to 80 mass% at a heating rate of 10°C min^{-1}.

The activation energy (Ea) of HAp crystallisation was determined by various methods using isothermal or non-isothermal conditions.

A non-isothermal method is experimentally easier than the isothermal method. Under non-isothermal conditions, the DTA or DSC curves are used to obtain Ea values from peak temperature measurements at different heating rates. Although many mathematical equations have been proposed for the calculation, the Kissinger equation (1956) is the most commonly used. The activation energy values for the crystallisation were estimated using Kissinger equation (1) through the changes in the temperature Tp (temperature at the maximum of crystallisation peak) with respect to the heating rate (Matusita, Komatsu & Yokota, 1984):

$$\ln\left(\frac{\phi}{T_p^2}\right) = -\frac{E_a}{R.T_p} + C \qquad (1)$$

where 'ϕ' is the heating rate (°C s^{-1}), Tp is the temperature corresponding to the maximum in DTA crystallisation peak (°C), Ea is the activation energy for mullite formation (kJ mol^{-1}), R is the ideal gas constant (8.314 J $mol^{-1}K^{-1}$) and C is a constant.



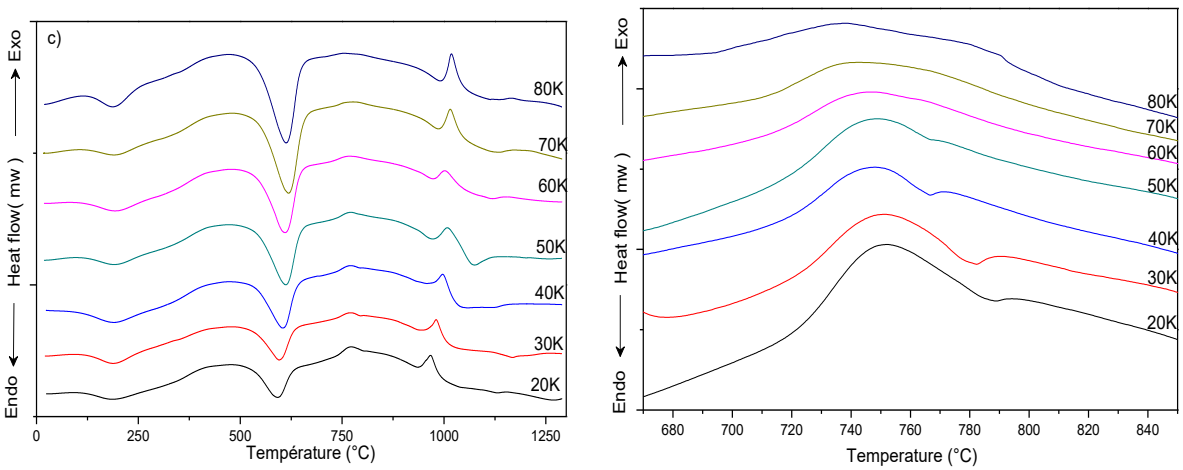
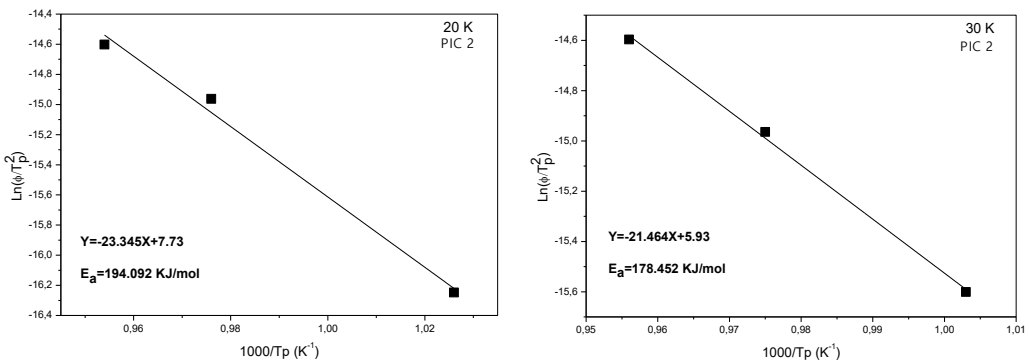


Figure 1. DTA curves of kaolin/phosphate compositions at a heating rate of a) 10°C min−1, b) 20°C min−1, c) 30°C min−1

Table 1. Crystallisation peak temperature (Tp/°C) from DTA results

Composite	Heating rate		
	10°C/min	20°C/min	30°C/min
20 K	732.3	752	771.8
30 K	722.1	751.1	770.2
40 K	724.5	748	771.3
50 K	720.3	751.6	772.9
60 K	720.2	750.2	767.5
70 K	717.4	749.1	775.5
80 K	714	737.5	753.5

The temperature is changed linearly with time at a known scan rate ϕ. A plot of $\ln(\phi/T_P^2)$ versus 1/Tp should be a straight line, whose slope yields the activation energy Ea for different compositions (Fig. 2)



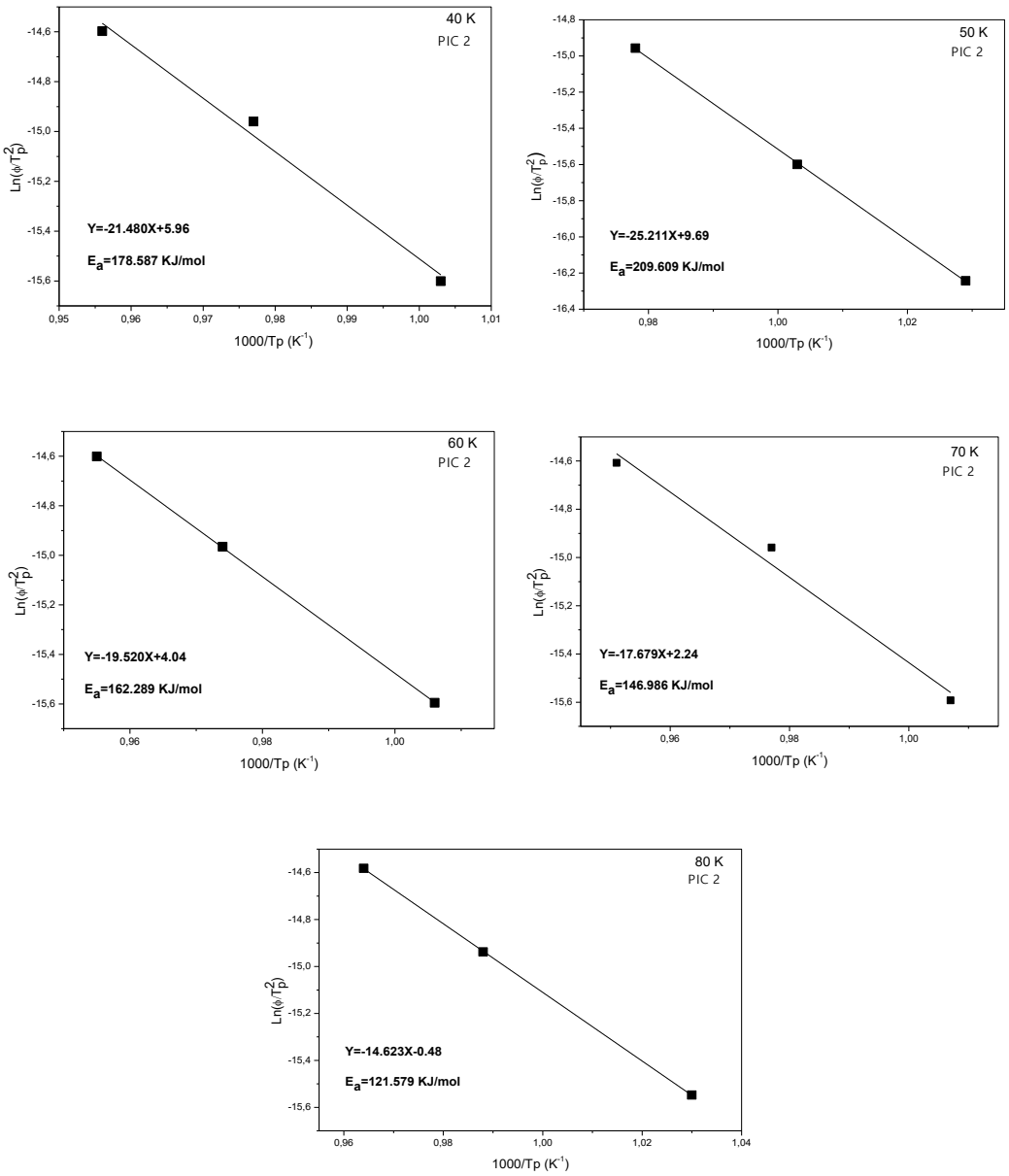


Figure 2. Plots of ln (ϕ/Tp) versus 1/Tp for 20, 30, 40, 50, 60, 70 and 80 K compositions

The activation energy as a function of percentage of kaolin is illustrated in Figure 3. The activation energy is explained as required energy to start a chemical reaction (Belhouchet et al., 2014). The curve shows a decrease in activation energy that can be attributed to the decrease in the amount of NP, and there is also a slight increase from 40% to 50% with a maximum value (209.6 kJ/mol) (Fig. 3). The activation energy of HAp is varied between 184 and 121 kJ/mol. Gross, Gross and Berndt (1998) found a higher value of the crystallisation energy of HAp (Ea = 274 kJ/mol). Feng, Khor, Liu and Cheang (2000) show that the activation energy of the crystallisation of HAp developed from an amorphous tricalcium phosphate is in the range of 198–268 kJ/mol.

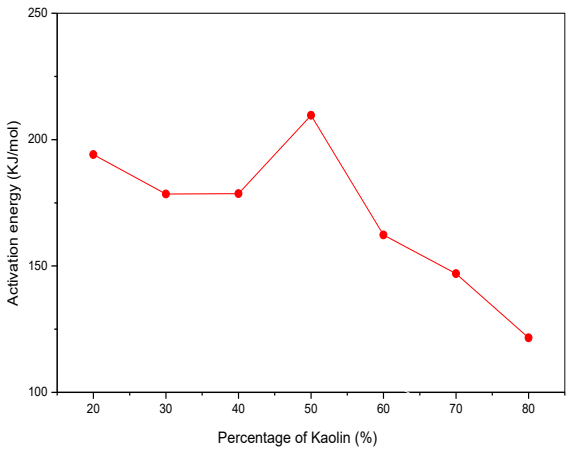


Figure 3. Variation of activation energy as a function of percentage of kaolin

4. Conclusions

The crystallisation kinetics and mechanisms of hydroxyapatite formation in different kaolin–phosphate compositions were investigated by DTA under non-isothermal conditions.

The difference in activation energy found by various authors may be partly due to different crystallisation processes and partly to different experimental conditions used.

The non-isothermal activation energies obtained from the DTA curves of 20, 30, 40, 50, 60, 70 and 80 K composites were found to be 194.09, 178.45, 178.58, 209.6, 162.28, 121.57 and 146.98 kJ mol^{-1}, respectively.

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