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Examination Synthesis Kinetic of Fluor Apatite with Using Free Model (TG) and Kissinger Method

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Abstract. In this Research The effect of additional F^{-1} ion in hydroxyapatite and convert that to Fluor apatite had been examined and after that Flourapatite synthesis kinetic with the aim of is conversional free method in the non-same temperature condition had been examined. For this matter we used (TG) experiment in 3 heating rate 7, 10, 15 (ºC) on minute. The activation energy of crystallization has been calculated in the frame of Kissinger model. And also for determination reaction mechanism and kinetic parameters we asked the activation energy (E) and reaction fraction (α) for assistance. After determined the (α) we can to suppose the reaction mechanism.

Keywords: Free model TG, Kissinger method, Fluor apatite, hydroxyapatite

1. Introduction

In the recent years, a lot of researches had been done about the kinetic investigation of thermal analysis. This researches are more important from two aspects; at the first kinetics, information's is necessary for modelling of each type of device that thermal decomposition occur in it and from second aspect kinetic are in relation with the mechanism of the process [1]. Knowledge about mechanisms, produce extraction of kinetic equations. However, we can do scientist studies in different instruments but weight measuring (TG) is a usual method that we use. In recent 20 years ago most investigation had been done about artificial apatite's using of artificial apatite's such as bioactive hydroxyapatite $(OH_2)6(po_4)10(Ca)$ to be expanded in density, and reason of this case is the similarity of materials from the viewpoint of crystalicaly structure and chemical composition with mineral texture of bone [2]. Bioactivity of this materials will be able them to make direction bond with damaged texture. Hydroxyapatite properties such as bioactivity, mechanical strength, solubility and capability properties can be optimum from method of chemical composition control, morphology and the grains size control [3]. Solution of Hydroxyapatite can be control by many so factors for example: rate of crystallization, chemical composition and elements stoichiometry ratio. One of the appropriate ways to reduce solubility rate is replacement of OH^{-1} groups in hydroxyapatite structure with F^{-1} ion that lead to form new composition that had named flour hydroxyapatite. This exchange ionic to increase crystallization, reduce strain crystically and at the end lead to chemical and thermal stability of structure. The important point in this replacement is control the amount of entering F^{-1} Ion into the structure. Hydroxyapatite use in restoration of bony defects in the form of condensed, but because of low mechanical properties for example high elasticity coefficient and brittle we can't use it under high loading operations. One of the important things is low thermal stability of hydroxyapatite that may be lead to differ in chemical composition. One of the advantages of flour Hydroxyl apatite is high thermal stability .in usage of flour Hydroxyapatite as powder with attention to type of application and properties to expect us able to find optimum amounts of mechanical properties, bio stability and bio annihilation with control the amount of entering ion into the structure [3,]. One of ways to produce this material is below equation, at first equation calcium phosphate produced and then had reacted with base fluoride material.

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$$3Ca_2+ + 2PO^{3-}_4 \rightarrow Ca_3(PO_4)_2$$

$$3Ca_3(PO_4)_2 + CaF2 \rightarrow 2Ca_5(PO_4)_3F$$

Pure fluorapatite has more chemical and structural stability than hydroxyapatite and forms the outer layer of teeth [4,5,6,7]

Application of free model method in the examination of non-same temperature kinetic had been started from 60 decade. Also we can do kinetic examination with different instrument but (TG) weight measuring is most usual method. In The (TG) experiment with differ in sample heating rate mechanism of reaction will not differ. Then mechanism of reaction is independent from heating rate of sample .with this assumption reaction rate is only dependent on temperature. Do in 3 different heating rate.

2. Materials and Method

In this investigation we used the $CaHPO_4$ powder with 98% purity from Germen Merk Company (102203), calcium fluoride from German Merk (1450894) and also used calcium hydroxide from German felokay with upper than 96% purity. For homogenize powder mixture we used the FP4 model planet ball mill .Because of that Flourapatiteis bio material, utensile that selected is producted from polyamide and balls selected produced from zirconia. Then we do the (TG) experiment on the mixture sample. For this experiment we used the (TGA401 Sanatara) device. In this (TG) method experiments had done in 3 heating rate β_1=7, β_2=10, β_3=15 degree on minute. With derivation from (TG) curve

we can calculate $\left[(\frac{d\alpha}{dt})\right]$ in different α and to drawing $(\frac{d\alpha}{dt})$ curve according to temperature and for per α in different heating rate to drawing amounts of $\ln\left[\beta_i(\frac{d\alpha}{dt})_\alpha\right]$ according to $\frac{1}{T}$ and at the end will calculate activation energy from line slope because slope is equal to $(\frac{-E}{R})$. The most usual method to heating the sample is that sample until early temperature like (T0) heated and experiment starting with fixed heating rate like as β. than we can to calculate sample temperature like as bellow equation $T = T_\circ + \beta.t$.

2.1. Results and Discussions

At the Fig 1 (TG) curve show the Flourapatite kinetic. With attention to the curve observed that in the temperature between 651ºC until 760ºC we have differ in slope, after examination observed that temperature for start the reaction is 650 ºC.

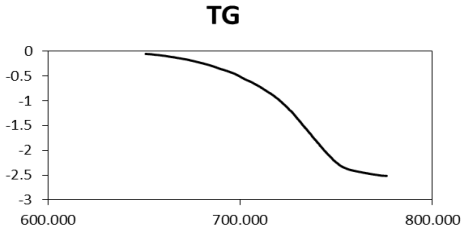

Fig. 1: TG Curve.

For calculate the kinetic parameters at the first determined the amount of α with asked the (TG) curve assistance. Fig 2 show reaction progress fraction in the 3 reaction rate (β_1,β_2,β_3).

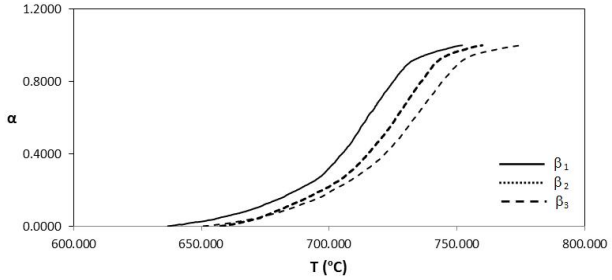

Fig. 2: Reaction progress curve in 3 reaction rate (β_1=7, β_2=10, β_3=15 degree on minute).

Table 1: reaction progress fraction temperature in different reaction rates (ºK).

α	β1	β2	β3
0.1	671.34	628.274	685.421
0.2	687.442	697.334	701.608
0.3	698.494	708.283	713.346
0.4	705.002	715.270	721.933
0.5	710.325	721.289	728.134
0.6	714.892	726.204	633.629
0.7	720.145	730.969	738.712
0.8	725.177	736.097	744.450
0.9	731.030	741.441	750.761

With attention to the above curve determined that with increase the heating rate starting and ending temperature of the reaction will increase and also all 3 Curve in the final temperature don't have any progress in the reaction fraction. In below table 1 temperatures that are in relation to the reaction progress fraction in reaction rate of β_1, β_2, β_3 determined. From Fig 2 curve, temperatures that are in relation to the heating rates of β1, β2, β3 in reactions progress fraction between 0.1 until 1 determined .and also drawing $(\frac{d\alpha}{dt})$ curve according to temperature (Fig 3).

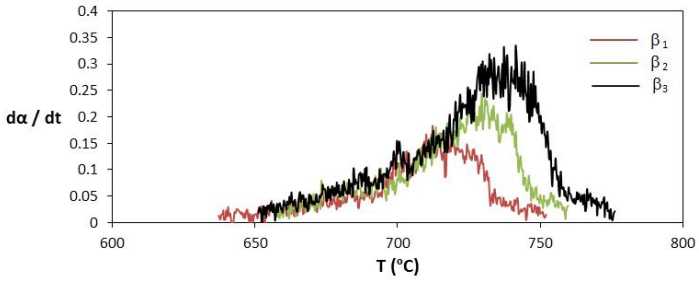

Fig. 3: $(\frac{d\alpha}{dt})$ According to temperature curve.

From above curve observed that with increase the heating rate maximum $(\frac{d\alpha}{dt})$ is in the more temperature. And then for each α amounts of $\ln\left[\beta_i(\frac{d\alpha}{dt})_\alpha\right]$ in different heating rates determine and drawing according to $\frac{1}{T}$ (Fig 4).

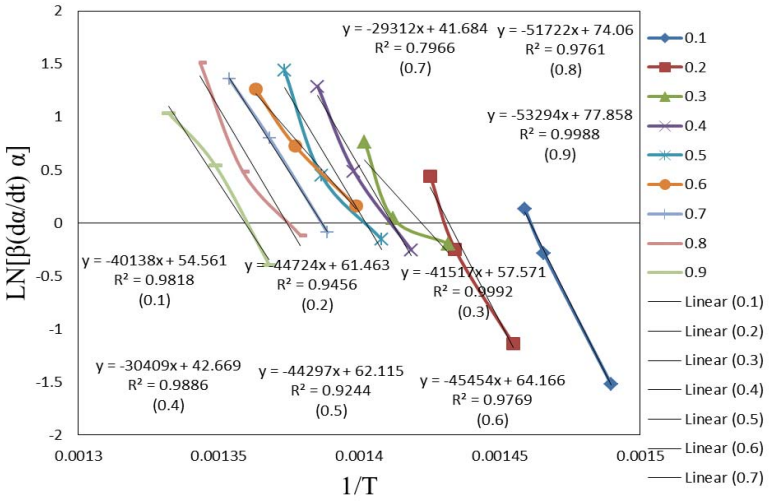

Fig. 4: $\ln\left[\beta_i(\frac{d\alpha}{dt})_\alpha\right]$ according to $\frac{1}{T}$ Curve.

The slop of curves showing that with use we can find activation energy.

α	E	R^2
0.1	79754	0.9818
0.2	88866	0.9456
0.3	82494.279	0.9992
0.4	60422	0.9886
0.5	88018.139	0.9244
0.6	90317.098	0.9769
0.7	58242.944	0.7966
0.8	102771.614	0.9761
0.9	105895.178	0.9988

3. Result

From above investigations to conclude if we use the (TG) curve for kinetic analysis thermal degree defect don't have high effect on the activation energy. With increase in activation energy the percent of defect increase and with increase temperature the percent of defect will be reduce.

With attention to the amounts of activation energies for different (α) that are different, it is showing that exchanging model and or reaction exchange. in above table observed that in 0.3 and 0.9 we have most agreement but in 0.9 activation energy is not desirable than 0.3 is the best and reaction mechanism follow than that, and we can to suppose the governer model in reaction with determined the best (α) with attention to below equation we can to calculate f(α) and after that suppose model than after calculations model of the mechanism is one dimensional diffusion.

$$f(\alpha)=\beta \left(\frac{d\alpha}{dt}\right) \alpha \diagup A\alpha EXP(-E/RT)$$

4. Reference

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