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Isothermal and non-isothermal crystallization Kinetic behavior of zinc-ferrite formation in the Low temperature flow injection co-precipitation synthesis reactor

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Abstract

The kinetic behavior of zinc -ferrite crystallization process has been studied by co-precipitation of chlorine salt and alkaline solution. Either the parameter of temperature rate variation, pH previous of reactant and pH alkaline solution results non isothermal process was described by Ozawa equation,. There are significantly deferent in the taking both isothermal and non isothermal data. In the non- isothermal there are just one experiment can be sufficiency to reveal any crystal forming parameters but in the isothermal needs several different temperature experiments to reveals the parameter of crystal forming . In this research have be done one time non -isothermal experiment at means temperature 40 ^{0}C with temperature increase from 49 ^{0}C to 53 0C, and four time isothermal experiments at means temperature 60 ^{0}C,70 ^{0}C and 80 ^{0}C respectively. The sampling of experiment data have be done effectively using pH real- time video data logger. As a result the energy forming of the zinc ferrite both isothermal and non-isothermal are -4.27kcal/.mol ,5.61kcal/mol respectively. The other kinetic parameter of crystallization and crystalline mechanism of both processes will be discussed.

Keywords: *co-precipitation, zinc-ferrite, non-isothermal process, crystallization, crystalline mechanism, data logger, kinetic behavior, flow injection co-precipitation synthesis.*

1. Introduction

Ferrites have been studied since 1936. They have an enormous impact over the applications of nano magnetic particles-NMP has opened the door for completely new technologies [1]. The ferrites NPM behavior have been revealed since Robert Kaiser at Avco-Nasa Corporate 1961 explore of ferrofluid successfully [2] at room temperature, can widely use depend on their chemical compose and the range of particle size. The Iron oxides in nano-scale have exhibited great potential for their applications as catalytic material [3,4] was recognized as arrange more NPM.

The material magnetite is one of basis forming NMP ferrite [5] is recognized as co-precipitation synthesis product, in this research will be try to reveal behavior of reaction dynamic from reaction data logger mainly the temperature and pH data has been recorded which is all of the series instrument display such as both thermometer and pH meter were recorded spontaneously. They have low eddy current losses and high electrical resistivity, or ferrite as nano materials are considered as both useful any gas sensor substance, semiconductor mother materials and catalyst substance [6].

A lot of method have been developed to form of ferrite material such as; high- energy grinding, plasma flame pyrolysis, electro-chemical, high thermal evaporation, hydrothermal preparation, sole gel, co-precipitation and etc. One of easy, simple and economical process is co-precipitation. The non-popular reason of not using co-precipitation method is the size of co-precipitation yield tend to wide distribution or tend to poly disperse crystal. One of advantage co-precipitation method is the process parameter can be observed and easy to trace [7].

1.1 Theoretical Basis

Flow Injection Synthesis is one way to do co-precipitation synthesis which can be done

automatically by using a data acquisition system supported datalogger instrument completed both high resolution of the digital pH meter and digital thermometer. In this study the data acquisition could be used to expected the necessary of performing material parameter such as the activation energy of crystallization, particle size, reaction rate, isothermal or non-isothermal reaction and especially to get activation energy of Cu-Zn Ferrite.

Thermodynamics of Zn ferrite behavior have been observed by many scientists since an intensively in the University of Michigan [8] use sophisticated calorimeter. At room temperature is 5.367 [cal/mol] [8]. According to Zn ferrite as co-precipitation yield of chlorine Zn^{2+}, $Fe^{3+}$and Fe^{3+} to alkaline hydroxide as precursor, the metal salts are in the negligible side, causing by suggest that all of input compound completely be amount of yields, but not in precipitant solution, the solution concentrate decrease proportional with increasing of yield concentrate [8], such as equation

The Zinc Ferrite yield formula is Zn Fe_2O_4, and measured in the solution system were mixed of metal salts raw material and alkaline any excess liquid. Fraction of yield can calculate as equation:

$$\%Yield = \frac{\Delta Cpr_t}{\Delta Cpr_\infty} = \frac{Cpr_0 - Cpr_t}{Cpr_0 - Cpr_\infty} = \frac{10^{-pOH_0} - 10^{-pOH_t}}{10^{-pOH_0} - 10^{-pOH_\infty}} \quad (1)$$

C_{pr_0} *is concentrationo of previous yield solution*
C_{pr_t} *is concentrationo of real time yield solution*
C_{pr_∞} *is concentrationo of steady state yield solution*
Ph_0 *IS pH of previous yield solution*
pH_t *is pH of real time yield solution*
pH_∞ *is pH of steady state yield solution*

If the equation 1 as isothermal process, it can be involved with Avrami equation, such as yield- %Y stated by equation 2, mainly

$$\%Yied = 1 - \exp(-k.t^n) \quad (2)$$

For simplifying assumption that the particle form is spherical, then if the growth rate particle is v, n is around 3 the k relation of v by simplifying, is $k = \frac{4}{3}\pi N v^3$. In other relationship v as a function of environment temperature that can be written in the Arrhenius equation, mainly v=B exp($-Q_E$/RT). B is constant. For *%yield = 0.5* , $t_{0.5}=(0.17/N)^{1/3}.(v)^{-1}$, then $Exp(Q_{E/RT})=K.(t_{0.5})$ where $K=B.(N/0.17)^{1/3}$, Furthermore obtained usefully equation 3 to reveal activation energy, mainly.

$$\frac{\partial(Ln\, t_{0.5})}{\partial(\frac{1}{T})} = \frac{Q}{R} \quad (3)$$

Where Q is activation or forming of crystal energy, R is gas constant.

The equation 1 was associated with both a reduction of the energy solutions and Arrheneus crystal formation of yield energy. If the equation 1 can be involved with non isothermal process, the yield could be stated with Ozawa equation, such as

$$\%Yield = 1 - \exp[-Z_t.t^n] \quad (4)$$

where Z_t is the rate constant of the non-isothermal crystallization process, Z_t and n are functions of the cooling rate α. Neither Avrami nor Ozawa equation have vulnerabilities that are complementary to the combine equation that will be more applicable generally. The advantage of Avrami-Ozawa behavior using to solve energy formation of yield is the equation realistic then perfect instead.

The combination of Avrami with Ozawa equation involved with perfection of the crystallization rate and energy formation such as [9];

$$Ln.K_C + n\,Ln.t = LnK_T - m.LnD \quad (5.a)$$

Where

$Ln\,K_c = \frac{\ln k}{\alpha}$; $k = \frac{4}{3}\pi.N.v^3$,

v *as particle growth rate* ;

$\alpha = \frac{dT}{dt}$ *as heating or cooling rate.*

D parameter link with equation

$$LnD = \frac{1}{m} Ln\,\{\frac{K_T}{K_C}\} - \frac{n}{m} Ln\,t\,, \quad (5.b)$$

by defining φ=n/m the ratio
Avrami Ozaw exponent, and

$F(T)=\{K_t/K_c\}^{1/m}$ [9]

Calculate of any LnD use the following equation,

$$Ln\,D = Ln\,F(t) - \varphi Ln\,t \quad (6)$$

The Ozawa equation relates of the %Yield with α, while The Avrami equation relates of the %Yield with t , then the relation t of α describe by equation

$$t = \frac{(T_i - T_f}{Abs(\alpha)} \quad (7)$$

T_i *is the initial temperatur*

T_f *is the temperature at time t*

In the real time data recorder the basis of the wet reaction parameter such as pH of solution and temperature could be recorded automatically at every time since the reaction continue.

The execution of activation energy use Avrami-Ozawa equation mathematically restricted by negative cooling rate (α). For the segmental reaction calculate with the temperature differential of reaction time, but abs(α) have to calculate for all segment with use cooling or heating rate estimation chart of Log α = Log F(T) – b log t.The activation of forming energy could be used the modification Ozawa equation such as

$$\log\left(\frac{abs(\alpha)}{T^2}\right) = -\frac{Q_{Ec}}{RT} + const \quad (8)$$

Determination of either Exothermic or Endothermic process can be seen by the value of overall temperature exchange rate that estimated by chart of Log α = Log F(T) – b log t. Negative value of α means the process is exothermic, and vise versa means the process is endothermic.

I.2 Calculation And Table Compilation Of Avrami-Ozawa Parameter, Extracted From Video Data logger.

The Flow Injection Synthesis of co-precipitation process is done by means of the acid alkaline titration. Here the alkaline solution is pumped with a peristaltic pump and injected into an acid solution which is in the tub. During the titration process reactant solution was stirred with a mechanical stirrer at a speed of 500 RPM.

The table of Avrami-Ozawa parameter compilation specifically of process parameter at vary temperature, include time of process, pH yield solution, rate of temperature exchange were extracted from data logger.

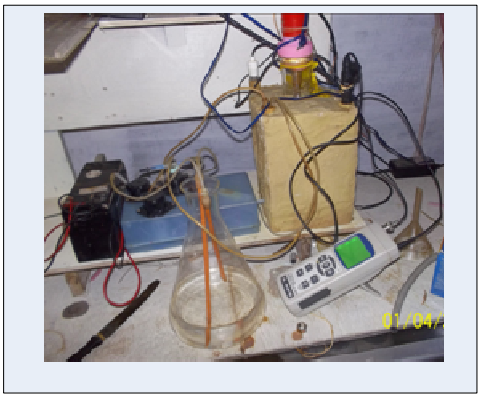

Figure 1. The picture of the flow injection synthesis of CuZnFerrite co-precipitation reactor with datalogger of pH and temperature acquisitions \

2. Experimental Details

2.1 Sample Raw Preparation.

The number of sample at this research required at least 4 samples, tree samples for isothermal process, one sample for non-isothermal, thus of all four samples have the same characteristics. All chemical reagent were analytical grade from MERCK and used as received without further treatment such as; $ZnCl_2$, $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, and sodium hydroxide (NaOH). With

$$2(1\text{-}x)FeCl_2.4H_2O + 4\ FeCl_3.6H_2O + 2x.ZnCl_2 + 16\ NaOH \rightarrow 2\ Zn_xFe_{(3-x)}O_4 + 16\ NaCl + (40\text{-}8x)\ H_2O \quad (7)$$

The yield are; $Zn_x\ Fe_{3-x}\ O_4$ with x certainty at $0<x<1$, were prepared by aqueous solutions of $ZnCl_2$, $FeCl_2.4H_2O$ and $FeCl_3.6H_{2O}$ in their respectively stoichiometry (60 ml of solution containing $ZnCl_2$, $FeCl_2.4H_2O$ and of 1M $FeCl_3.6H_2O$) were mixed thoroughly about 50°C and this mixture was added to the solution of NaOH (0.55 M dissolved in 800 ml of distilled water. The yield solutions were decanted and washed interchangeably several times with deionizer water. The partially of yield adding poly ethylene Glycol (PEG) 4000, then dried at room temperature. The dried powder was grounded thoroughly in a clean agate mortar. The ground powder was then pelletized using hydraulic press. The structure and crystallite size were determined from the X-ray diffraction (XRD) measurements use of Philips (Pw/1835) X-ray diffraction meter with CuKα (λ = 1.5406 Å) radiation.

3.Result and discussion

3.1 Estimation of the activation energy crystallization use Avrami behavior of isothermal chemical reaction- method.

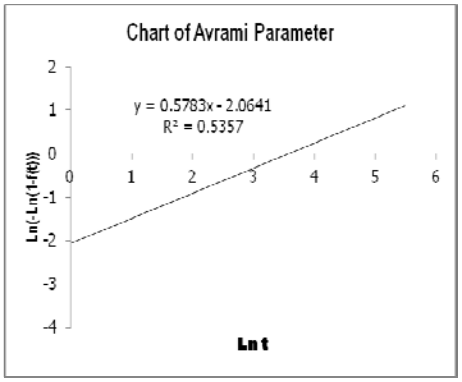

Figure 1.b. The chart of the ZF60 Avrami parameter were found n=0.578, k=2.064

All of data are then processed by isothermal of following order such as; calculations and tabling of the yield formation, graphing of Zn-Ferrite sigmoid, fitting of half time of yield-$t_{0.5}$, and etc.

The changing of the pH yield solution at 60^0C is from 13.36 to 12.53 and from 12.68 to 10.81, at 70^0C is from 12.70 to 9.97, and at 80^0Cis from 12.16 to 11.16 respectively. All of the parameter processes was recorded at span of 2 second .

For the practical purpose, the calculation was prepared in the following table; Table 1. The activation energy crystallization of Avrami estimation methode At the same proceed can be found the Avrami parameter of couple temperature and pH from experiment data such as the following table 4.

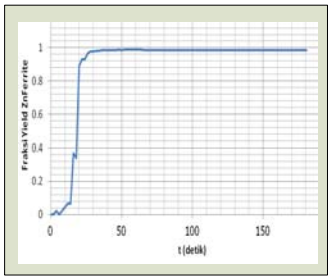

Figure.1 Graph of Sigmoid ZF60, $t_{0.5}$=18{(0.5-0.34)/(0.89-0.34)}x(20-18) =18.58 sec

Table 4. The Avrami parameter of isothermal coprecipitation reactioan at around 60,70,80 ^{0}C temperature.

Temperature	pH awal	k	n	T [K]	t 0.5 (Sec)	1/T	Ln t 0.5
60	13.36	0.1269	0.5783	326	14	0.0030675	2.6390573
60	12.68	0.17035	0.1306	330	19	0.0030303	2.944439
70	12.7	23.1	1.403	348	23.1	0.0028736	3.1398326
80	12.16	0.7990	0.357	357	24.42	0.0028011	3.1954025

From Table 4, column 7 (1/T) and 8 (ln $t_{0.5}$ can be made chart of Ln $t_{0.5}$ versus 1/T. The chart function is used to estimate activation energy as the follow;

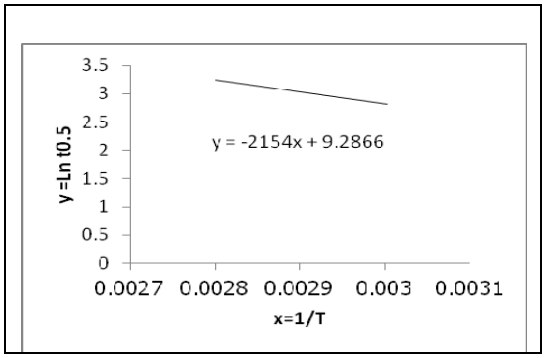

Figure 4. The trend Linier chart of Ln(-Ln(1-f(t)))as Y Versus ln t as X. Trend Linier result Y=-2154 X + 9.2866 .

The Avrami methode estimate the activation energy formation of Zin Ferrite is -2154x 8.31 J/mole = 17.90 kJ/mol=-4.27 kcal/mol.

3.2 Estimation of the activation energy crystallization use method of Avrami-Ozawa behavior of non-isothermal chemical process.

Preveously the data of both pH and temperature are extacted frome datalogger and were followed by making columns of data such as; fraction of yield Y(t), temperature K, logaritmic of (1-Y(t)),or Log(-Ln(1-Y(T), real time of heating or cooling rate α.

a) Chart of Avrami parameter estimation

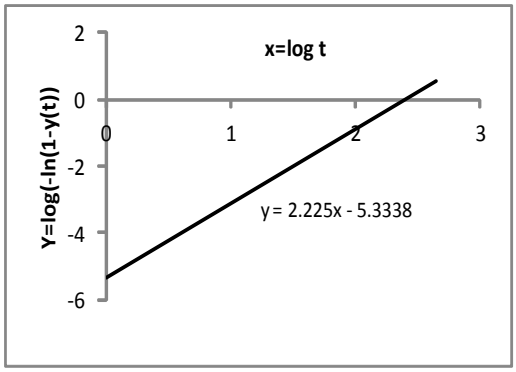

Figure 5. Plot of Log(-Ln(1-y(t))) vs.log t

The Avrami equation
Log[-ln(1-y(t)]=log k +n log t
From the chart is found
y=2.22X-5.33

That's means parameter of Avrami are;
n=2.22, log k = -5.33 k=213.80,

b) The chart of Ozawa parameter estimation

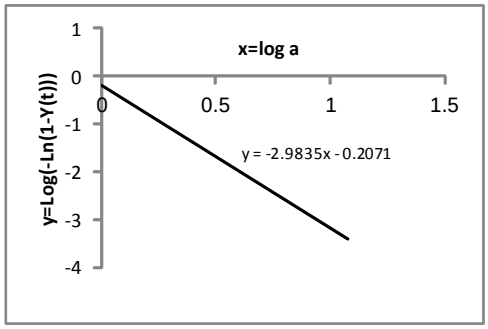

Figure 6. Plot of Log(-Ln(1-y(t))) vs. log a

The Ozawa equation.
Log[-ln(1-y(t))]=log K(T)-mlog(α)
From the chart is found
Y=-2.98 x – 0.20
The Ozawa parameter are ;
m = 2.98 K(T)= 10^0.20=1.58

c) The chart of overall heating or cooling estimation.

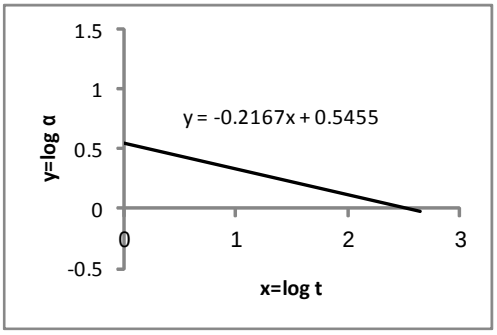

Figure 7. Plot of Log α vs. log t

The overall of cooling or heating rate estimation
Log α = Log F(T) – b log t
Or
y = -0.22 x + 0.5455,
b=-0.22 , F(T)= 3.512.
$K(T)/K(c)= F(t)^m=(3.512)^{2.98}=42.24$
α = log k/logKc; K(c)=1.58/42.24=0.003
we find that α=(-5.33)/-2.52=2.12
The overall heating rate = 2.12 [^{0}C/minute]

d) The estimation of Activation energy

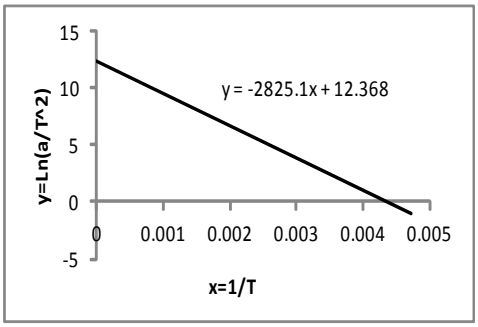

Figure 8. Plot of $Ln(a/T^2)$ vs. 1/T

The Avrami-Ozawa methode estimate activation energy forming of zinc ferrite is 2825x 8.31 J/mole = 23.48 kJ/mol=-5.61 kcal/mol.

3.3 The Estimation of activation energy crystallization use X-Ray Diffraction by Riettvelt analysis method.

The estimation of the energy content of material require information of the basic enthalpy all of the elements that built of the material compound. One of the non destructive ways is X rays diffractions analysis continued with the structural refinement by *Rietveld* method. In the table 6 below the results of the Zn Ferrite element content XRD analysis were prepared.

a) ZF60 Sample

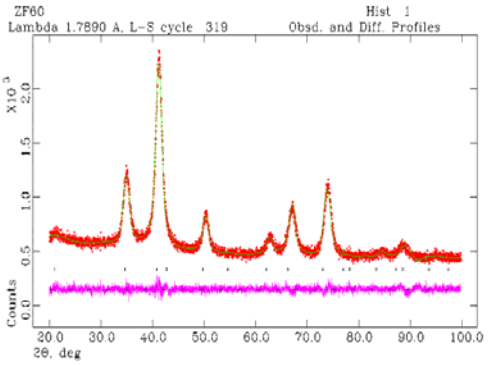

Figure 9 . X-ray diffraction pattern of ZF60

With the reference of cation distribution of Zn and Fe result the non stoichiometri formula of sample zinc ferrite ZF60 is $Zn_{0.4091}Fe_{2.5909}O_4$.

b) ZF70 sample.

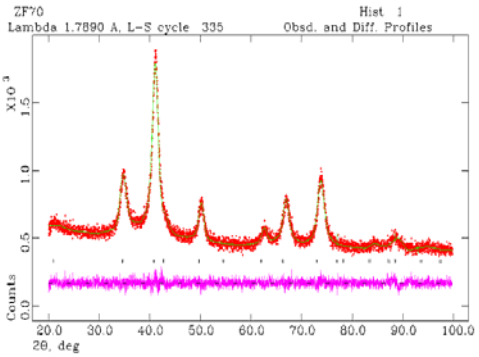

Figure 10.X-ray diffraction pattern of ZF70 .

The non stoichiometri formula of sample zinc ferrite ZF70 is $Zn_{0.416}Fe_{2.584}O_4$

c) ZF80 sample

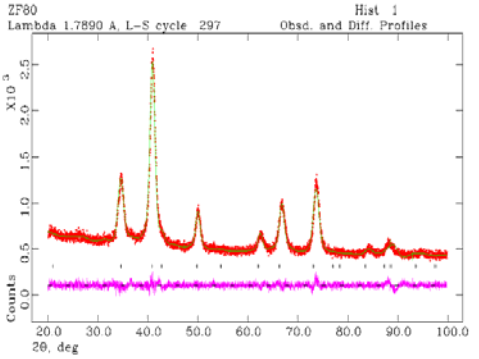

Figure 11 X-ray diffraction pattern of ZF80

The non stoichiometri formula of sample zinc ferrite ZF70 is $Zn_{0.412}Fe_{2.588}O_4$

The calculation of energy compoud forming could be done by addition process all of the elements enthalpy, then the enthalpy of the material depends on the degree inversion of every elements built compound of material. It's will be obtained from the structural refinement by the Rietvelt method of XRD analysis as follows;

a. ZF60= $Zn_{0.409}Fe_{2.591}O_4$

$$H^0_{ZF60} = 0.409x\Delta H^0_{ZNO} + 0.59 kH^0_{FeO} + 2xH^0_{Fe2O3}$$

$$= (0.409x3.504 + 0.59 kx2.720 + 8.24 =$$

$$11.283 \ [kJoule/mol] = 2.696 \text{kcal/mole}$$

b. ZF70= $Zn_{0.416}Fe_{2.584}O_4$

$$H^0_{ZF70} = 0.416xH^0_{ZNO} + 0.584xH^0_{FeO} + 2xH^0_{Fe2O3}$$

$$= (0.409x3.504 + 0.564x2.720 + 8.24 =$$

$$11.496 \ [kJoule/mole] = 2.747 \ kcal/mole$$

c. ZF80= $Zn_{0.412}Fe_{2.588}O_4$

$$H^0_{ZF80} = 0.412xH^0_{ZNO} + 0.584xH^0_{FeO} + 2xH^0_{Fe2O3}$$

$$= (0.412x3.504 + 0.584x2.720 + 8.24 =$$

$$11.272 \ [kJoule/mole] = 2.694 \ kcal/mole$$

As a result the average of the zinc ferrite standart enthalpy (H^0_{ZF}) and the enthalpy of ZnFerrite at 298^{0}K (H^{298}_{ZF}) is 5690.9 cal/mol cccordig with Edgar. F research [12]. the energy forming or activation of crystallization energy ($\Delta H = H^{298}_{ZF} - H^0_{ZF}$) is 2.99 kcal/mol

Table 5. Comparison of different method

Method	Energy [kcal/mole]	Thermal behavior
Avrami	4.27	exothermic
Avrami-Ozawa	5.61	exothermic
XRD analysis	2.99	As a refference

The different analysis due to amongst other things, the calculation of the measurement system does not include external energy processes such as stirrer energy and the environmental energy, this is caused the adiabatic nature of the co-precipitation process is not achieved. The stirrer process contributed to the temperature increased. An estimated the stirrer energy of isothermal co-precipitation-Avrami process, around 1.28 [kcal/mole], where as in the measurement process of the non-isothermal Avrami-Ozawa is around 2.62 [kcal/mole]. The Avrami-Ozawa dominance of the Avrami show that inequality occurs likely by the end of the process [10,11].

This experiment did not use the thermodynamic apparatus such as differential scanning calorimeter (DSC), then the co-precipitation reactor is considered to be working as DSC need to be examined carefully . The rate of change of temperature at any time as different temperature to peak temperature of different time in minute in span of the peak temperature acquires [11] .

The particle size of Zinc Ferrite can be maintained without agglomeration effect after synthesis in form of *ferrofluid* where each of the Zinc Ferrite particle coat by surface active substance [12]. According with thermodynamic analysis, the enthalpies formation of the Zinc ferrite 2-3 spinels around -2 till – 5 [kcal/mole] [13,14], This means that the experiment can be considered successful.

The Avrami behavior analysis in this experiment has weakly to the averaging of temperature process as attempt to make isothermal system, but naturally the process is non-isothermal. The other aspect is difficult to regulate temperature stay on the stable level. This reason held on non-isothermal process the Avrami-Ozawa behavior was suggested to use as satisfy method to reveal the process activation energy, which are just one experiment require, and more simple process.

4. Conclusion

In the zinc ferrite co-precipitation synthesis , using both the Avrami and the Avrami-Ozawa method have been proved could be used to reveal the amount of the crystallization formation energy and expectation of the energy required of the synthesis.

Although there have to reveal many implicit co-precipitation process parameters before, such as; growth rates of crystal, nucleation rate and the number of nucleation, of the isothermal co-precipitation formulated by Avrami whereas dynamical process such as cooling or heating rate were revealed by the non-isothermal co-precipitation was formulated by Ozawa, both have been able to refine each other as Avrami-Ozawa behavior, all of it's need the suggestion that of all of reagent are perfect.

The key of the achievement co-precipitation synthesis is the understanding of the relation between the concentrate exchange of metal salt solution were be represented by the decreasing of sodium concentration solution with the result of yield formation, then the co-precipitation process require advance both pH meter and thermometer measurement that can be operated simultaneously. Successfully of this experiment is one of the new method through, that either the Avrami method or the Avrami-Ozawa method can be done either with or without the DSC thermodynamic apparatus, then require advance examination instead..

Using of Avrami-Ozawa method to expect thermodynamic parameter of process is more easy , simple and economic experiment compared by either Avrami or Ozawa method that needs some kind of trial at same temperature.

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