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Thermal Behavior of the Formation of the Zinc-Ferrite in the Flow Injection Synthesis Reactor

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ABSTRACT

In this research to estimate of the forming energy of Zn-Ferrite were used of the isothermal reaction by using Avrami equation and Avrami Ozawa for Non-Isothermal reaction in use Flow Injection Synthesis reactor, whether as Isothermal or non-isothermal. According the methods above can be obtainedthe formation energy of Zn-Ferrite. In this research have be done four time isothermal experiments at the temperature 60 ^{0}C,70 ^{0}C and 80 ^{0}C respectively. The sampling of experiment data have be done effectively using pH data logger where both pH and temperature were written in SD card memory automaticallyin form Excel format. As a result the formation enthalpy (ΔH) 4.2 kcal / mol with entropy (S) 12.6 cal / mol deg and 3:14 density gr / cc,respectively.

Introduction

Material forming especially according to both the enthalpi and entropy of the material parameters can determine the stability of crystalline materials. Either as a base an applied science Zn

Ferrites Iron Oxide is a popular ingredient both as the catalytic

the semiconductor and magnetic material. Such

the materials have a very great usefulness as a material that is Nano Magnetic Particle-NMP that open the doors of new technology. This material have been revealed when Robert Kaiser at Avco-Nasa Corporation at 1961 as nano material that explored of the Ferro fluid material successfully [1,2] The characteristic of this nano material beside depend on the chemical compose but also depend on the particle size range. The Iron oxides of Zn-Ferrite exhibited as great potential as catalytic material[3,4] was recognized as arrange more NMP. The magnetite (Fe_3O_4) is the parent material of ferrite. where the material also have the basis of Nano-Magnetic-Particle forming NMP [5]. Ferrite material is recognized as co-precipitation synthesis yield. In this works will be try to reveal behavior of the dynamic reaction by use pH data logger mainly Changes in the behavior of both the temperature and pH data has been recorded by pH data logger instrument which all of the instrument display such as both thermometer and pH meter were recorded spontaneously. Either as bulky material substances or powder material they are considered magnetic superior because as magnetic material core have low eddy current losses and high electrical resistivferany the pyrolysis, electro-chemical process, high thermal evaporation, the hydrothermal preparation, and sole gel, co-precipitation and etc. One of easy, simple and economical process is co-precipitation. One of the advantage co-precipitation method is the process parameter can be observed and traced easily [7].

For these reasons the flow injection technique (FIS) has been developed by the author for the synthesis applications Avrami-Ozawa equation practically in the laboratory.

Formulated Background.

Zinc ferrite- or in the chemical formula $ZnFe_2O_4$ have thermodynamics behavior that have been observed by many scientists since intensively in University of Michigan [8] use sophisticated calorimeter. That forming energy at room temperature of $ZnFe_2O_4$ is 5.367 [cal/mol] [8], where as precursor, the metal salts are in the negligible side, causing by suggested of all input compound completely be amount of yields, but not in the precipitant solution, where the solution concentrate will decrease proportional with increasing of yield concentrate [8], such as equation

$$\%Yield = Y = \frac{\Delta Cp_t}{\Delta Cp_\infty} = \frac{Cp_0 - Cp_t}{Cp_0 - Cp_\infty} = \frac{10^{-pOH_0} - 10^{-pOH_t}}{10^{-pOH_0} - 10^{-pOH_\infty}} \quad (1)$$

Where pH_∞ is steady state pH , pH_o is previous pH, pH_t is real time pH solution. Cp_0, Cp_1, Cp_∞ are concentrate of solution at previous, real time and at steady state.

Up to determined of the pH and process temperature the crystal forming energy can de estimated. There were several methods to estimation of its, mainly ; Hess law according to

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the chemical process, Avrami equation for isothermal process, Avrami Ozawa for Non-isothermal.

In this work try to describe the methods with the several data were gated from pH data logger of the co-precipitation process to forming the Zn Ferrite use Flow Injection Synthesis- *FIS* [9,10]

According idealism of crystallization energy, Hess Law say that the amount of heat needed or released in a chemical reaction does not depend on the course of the reaction but is determined by the initial and final states, therefore can be used as initial guidelines for initial crystal formation energy. Further study of the forming crystal energy use Avrami method for isothermal process, and continued using more general Avrami method in which the reaction system is non-isothermal process.

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

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

or as a function of the process time constant τ, at the time of the t process then the yield can be expressed as equation

$$[\%Yied] = 1 - \exp(-\frac{t}{\tau})^m \quad \ldots\ldots\ldots\ldots..(2.a)$$

The parameter "m" depend on the shape of the particle phase. The parameters value m are about 3, 2, 1 respectively illustrate the particle shape approaching balls, discs and rods. Combination of both equation 2 and 2.a may obtained the relation of between the parameter m and n as equation below;

$$\tau.k = t^{(m-n)} \quad or\ (m-n) = \frac{\log(\tau.k)}{\log(t)} \quad \ldots\ldots\ldots\ldots\ldots...(3)$$

The Avrami equation can be applied generally to other changes of phase in materials, like chemical reaction rates in constant temperature or isothermal, and may be extended to the non-isothermal crystallization. [11]

In generally, the Avrami equation can be written as a natural logarithmic function of the yield as logarithmic equation below,

$$Ln\{(1-Y(t)\}^{-1} = (\frac{t}{\tau})^m$$

Then $$Ln\{Ln\{1-Y(t)\}^{-1}\} = m.Ln(t) - mLn(\tau) \quad \ldots\ldots\ldots \quad (4)$$

In the practical field both the parameter Y(t) and t can be harvested from calculation of the pH function in time process t ,that automatically it can be gotten from memory of the pH data logger. Furthermore will be obtained the usefully of the equation 3 to reveal of the activation energy equation, mainly.

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 realistic equation.

The combination of the Avrami and the Ozawa equation will be involved by perfection of the crystallization rate and the energy formation such as ;

$$Ln.K_C + n\,Ln.t = LnK_T - m.Ln\,D \text{ [12] } \ldots\ldots\ldots\ldots\ldots (5).$$

Where the natural logaritmic of the K_c constant according to the equation of

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

v *as the particle growth rate* ;

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

or the temperature change every second

Calculate of any LnD use the following equation, energy yield. If the equation 1can be involved with the non isothermal process. [11]

Then the yield could be stated by Ozawa equation, such as

$$\%Yield = 1 - \exp[-Z_t.t^n] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

$$LnD = \frac{1}{m}Ln\{\frac{K_T}{K_C}\} - \frac{n}{m}Lnt$$

or $Ln\ D = Ln\ F(t) - \varphi Ln\ t$ ……..……(7)

by defining φ=n/m the ratio Ozawa then can be obtained that $F(T)=\{K_t/K_c\}^{1/m}$ [13]. The Ozawa equation relates of the %Yield with α, while The Avrami equation relates of the %Yield with t , then the relation t of with α describe by the equation of

$$t = \frac{(T_i - T_f}{Abs(\alpha)} \quad \ldots\ldots\ldots\ldots\ldots (8)$$

T_i *is the initial temperatur*

T_f *is the temperature at time t*

The equation number as the series of according to the time of the reaction process temperature. In the real time t the data recorder of the basis of the wet reaction parameter such as pH of solution and temperature could be recorded automatically at every time since the reaction is continue. By the equation reasons the forming crystallite energy can be traced use satisfaction both temperature and pH data, such as in this paper.

The equation 1 was associated both a reduction of the energy solutions and the Arrheneus crystal of the formation

$$\frac{\partial(Lnt_{0.5})}{\partial(\frac{1}{T})} = \frac{Q_E}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

Isothermal Process Equipment.

The Stirrer speed was used Optimal process temperature is set at $60\ ^0$ C, Caused by changes in the average temperature is about 3^0 or 5% of the average temperature of the chemical reaction process. Use of the reactor either on system FIS isothermal or non-isothermal should be done as quickly as possible to avoid heat accumulation will affect the actual temperature of the reaction .

Non-Isothermal Process Equipment.

The instrumentation system mainly; pH and temperature data logger, pH sensor, thermometer, the reactor equipment and instrumentation can be seen as figure 1 below

Figure1. The picture of the flow injection synthesis of the ZnFerrite co-precipitation [9,10] reactor with data of the pH and temperature acquisitions.

In the Figure 1 can be known the existent of both the main reactor, instrumentation data logger, sensors and peristaltic pumps as process control of the instrumentation holder.

The main difference between isothermal and non-isothermal reactor is a high thermal conductor for isothermal while high thermal reduce the non-isothermal ..

Calculation and table compilation of the Avrami-Ozawa parameters, extracted from pH datalogger

Table of the Avrami-Ozawa parameter compilation specifically of the process parameter at vary temperature, include both the time process, the pH yield solution, and the rate of temperature exchange can be extracted from the data logger have been recorded in the SD-Card and automatically have been stored in the form of excel office. Furthermore the data content can be moved from the SD card to the computer's memory and the data can be processed on excel data processing generally. In this process no data extraction activity be required. There are any couple of the linier chart and graph to converge of the activation energy of the material Ferrite.`

III. Experimental Process

The Preparation of the Sample

The preparation of raw materials prepared for the 4 types samples, which are useful for, among other things; 1 isothermal samples, 3 samples of non-isothermal. The four samples were blended in a blend of the same raw materials which are further divided into four sections that have the same weight All chemical reagent were analytical grade from MERCK and used as received without further treatment such as; $ZnCl_2$, $FeCl_2.4H_2O$ (99%) , $FeCl_3.6H_2O$ (99%), and sodium hydroxide (NaOH). With the chemical equation

$2(1-x)FeCl_2.4H_2O + 4\ FeCl_3.6H_2O + 2x.ZnCl_2 + 16\ NaOH \rightarrow 2\ Zn_xFe_{(3-x)}O_4 + 16\ NaCl + (40-8x)H_2$…… (10)

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 respective 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 dried powder was grounded thoroughly in a clean agate mortar. The ground powder was then pelletized using hydraulic press.

X-Ray Diffraction test

The structure and crystallite size were determined from the X-ray diffraction (XRD) measurements use Philips (Pw/1835) diffraction meter with electrode CuKα. the long wave X ray radiation λ = 1.5406 Å. The X-Ray Diffraction test purposes is to determine the composition of the atoms that build up of the material molecules, according with the *Hess law* where the net forming energy of molecule depend on all of the atomic energy to build of the Ferrite material molecule.

IV. Result and Discussion.

Estimation Of The Activation Energy Crystallization Use Avrami Behavior Of Isothermal Chemical Reactio Method.

All of the reactor process data is then processed by isothermal of following order such as; calculations and tabling of the yield formation, graphing of ZnFerrite sigmoid, fitting of half time of yield-t_{05} , and etc. The changing of the pH yield solution at 60^0C is from 13.36 to 12.53 and 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 use table of the following table; where at the same proceed can be found that the Avrami parameter of the series data of couple temperature and pH .

The content of the temperature and pH series were obtained from data sheet of the memory-SD card of the pH data logger. The chemical process data were also arranged as data Excel sheet. We have to replace it to the Excel table where the Avrami equation will be applied.For example the processing data were displayed at a temperature of 60 degrees C. The initial pH of the process is 13.36, can be obtained Sigmoide graphic image as the following figure. From the table the results obtained within 50% yield t0.5 = 14 sec.

From columns Ln {-Ln (1-Y (t))} and column L (t) can be plotted graph Avrami, accompanied by the line equation as figure 3 below.

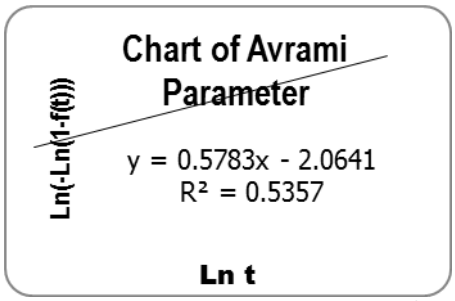

Figure 3. The chart of the ZincFerrite at 60^0C,as Yield Isothermal Process.

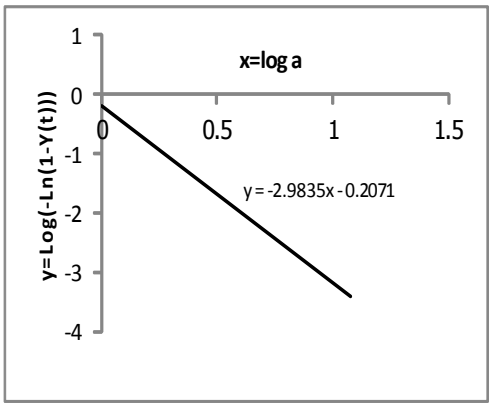

Figure 6. Plot of Log(-Ln(1-y(t))) vs. log a R^2= 0.67 [14] The Ozawa equation. Log[-ln(1-y(t))]=log K(T)-mlog(α), From chart is found Y=-2.98 x – 0.20.

The Avrami as equation Y= 0.5783 X+2.0641, R^2=0.5357. R=0.73. The Avrami parameter were found n=0.578, k=2.064

In the next work there are 3 series temperature and pH solution then obtained 3 Sigmoid graphs and 3 charts of linier trend of Avrami parameters. The series temperature are constant temperature 60^0C, 70^0C and 80^0C with the name of sample as FISAC,FISNET, and KONET respectively.

Table 4. The Avrami parameter of isothermal co-precipitation reactioan at around 60,[11] 70^0C.

Sample	k	n	T [K]	t 0.5 (Sec)	1/T	Ln t 0.5	Proces Description
60^0C	0.126	0.578	326	14	0.003	2.6390	Isothermal
FISAC	0.170	0.130	330	19	0.003	2.9444	Non Isotherm
FISNET	23.1	1.403	348	23.1	0.003	3.1398	Non Isotherm
KONET	0.799	0.357	357	24.42	0.003	3.1954	Non Isotherm

From the three series of the data shown herein discussion of the data is isolated at 600C. By the same analysis was also discussed forming reaction at temperatures of 700C and 800C.

From Table 4, column Ln (t 0.5) and the column 1 / t can be made linear graph that describes activation energy of crystal formation as Figure 3.1 below

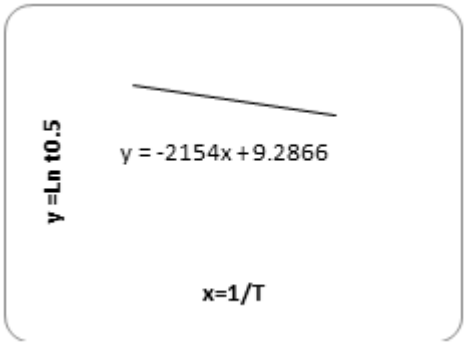

Figure 3.1 The chart of Ln($t_{0.5}$) versus (1/T).

The trend Linier result Y=-2154 X + 9.2866, where Ln(-Ln(1-f(t))) Versus ln (t) as R2=0.768 R=0.87 Its means that the activation energy crystallization of the Avrami methode is estimated -2154x 8.31 J/mole = 17.90 kJ/mol or -4.27 kcal/mol. Entropi S = 12,82 [cal/deg]

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

The activation energy crystallization of Avrami-Ozawa methode can be described in several of charts that obtained from main table mainly;

a. Linier trend of Log(-Ln(1-y(t))) vs.log t to obtain the Avrami parameter,

b.Linier trend of Log(-Ln(1-y(t))) vs. log a to obtain the Ozawa parameter,

c.Linier trend of Log α vs. log t to obtain cooling or the heating rate estimation

d. Linier trend of Ln(a/T^2) vs. 1/T to obtain activati energy crystallization of Avrami-Ozawa .

For purposes of comparison of the energy calculation methods were used the same tables and temperature. in this study appear to process at a temperature of 60^0C, The fact energy calculated also estimated at 70^0 and 80^0.C.

Step by step the calculation begins by displaying a graph and linear equation which is processed by Excel program such as the display on the figure 5

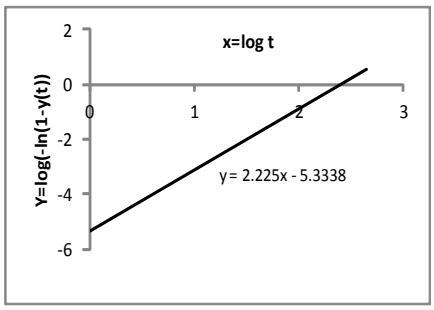

Figure 5. Plot of Log(-Ln(1-y(t))) vs log t [14].

The Avrami equation , Log[-ln(1-y(t)]=log k+nlog t From chart is found y=2.22X-5.33 R^2 = 0.84 That's means parameter of Avrami are; n=2.22, log k = -5.33 k=213.80, The next step to calculate the change of temperature parameter perminute Use the Ozawa equation with helping of the charts Log(-Ln(1-y(t))) versus log a as figure 6. Heating or cooling rate estimation use chart Log (a) versus Log(t)The Ozawa parameter are ; m = 2.98 K(T)= 10^0.20=1.58

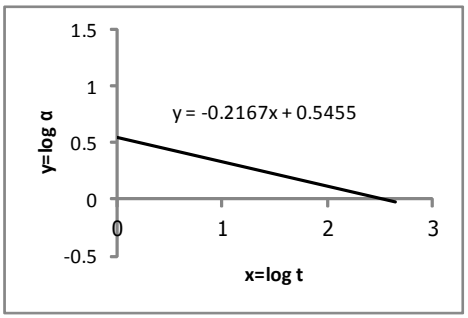

Figure 7. Plot of Log α vs. log t, The cooling or heting rate estimation Log α=Log F(T) – b Log t.

Or from the chart figure 7, obtained Y=-0.22 x +0.5455, it means b=-0.22, F(T)=3.512 R^2=0.84

Then K(T)/K(C) = F(t)^m = $(3.512)^{2.98}$ =42.24

K(c) = 1.58/42.24= 0.003

Heating or cooling rate α, where α=log k/ log K(c) Then α=(-5.33)/-2.52 = 2.12, heating rate = 2.12 [^{0}C/minute]

The next chart Kissinger used to estimate the activation energy as Figure 8 below;

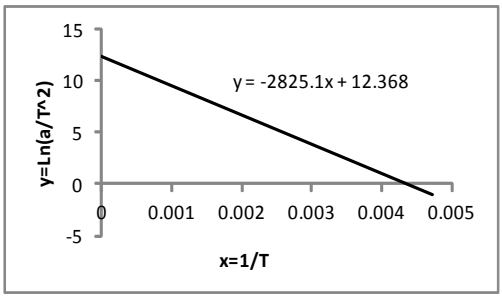

Figure 8. Plot of Ln{α/T^2} vs (1/TFrom the chart figure 8, obtained Ln{α/T^2}=-2825.1 (1/T) +12.368.

Or Y=-2825 x +12.368 R^2 = 1 it means pure linier.

The activation energy crystallization of Avrami-Ozawa methode is estimated is 2825x 8.31 J/mole = Q_E = 23.48 kJ/mol=-5.61 kcal/mol, as Activation Energy determined using Kissinger approach. Entropy S=5610/(273+75)=16.12 cal/deg.mol

The Estimation of activation energy crystallization use X-Ray Diffraction test and analysis by Riettvelt refinement 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 to elaborate of the atomic content in the solid state material is X rays diffractions continued by GSAS analysis with structural programe Rietveld refinement method Include In the table 9 below the results of the Zn Ferrite element content XRD analysis were prepared.

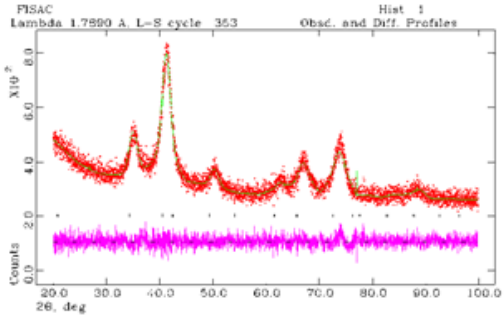

Figure 9 . X-ray diffraction pattern of FISAC Crystall Lattice Parmeter.

The result of Rievelt Refinement Analysis
a = 8.5092(1) Å, b = 8.5092(1) Å c = 8.5092(1) Å,
α = β = γ = 90°, V = 616.1(3) Å^3 ρ = 3. 221 gr.cm^{-3}
Zn =0.4091 Fe=2.5909
Non Stochiometri equation $Zn_{0.4091}Fe_{25909}O_4$

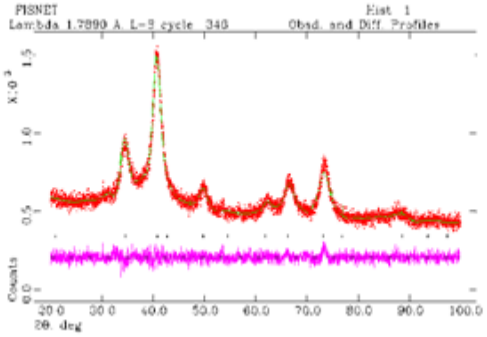

Figure 10 . X-ray diffraction pattern of FISNET.

The result of Rievelt Refinement Analysis obtain
Crystall Lattice Parmeter
a = 8.5092(1) Å, b = 8.5092(1) Å c = 8.5092(1) Å,
α = β = γ = 90°, V = 616.1(3) Å^3 ρ = 3. 02 gr.cm^{-3}
Zn =0.4158 Fe=2.5584
Non Stochiometri equation $Zn_{0.416}Fe_{2.584}O_4$

The graph of X-Ray Diifraction after smoothing by Rieltvelt refinement method of Sample Lable KONET

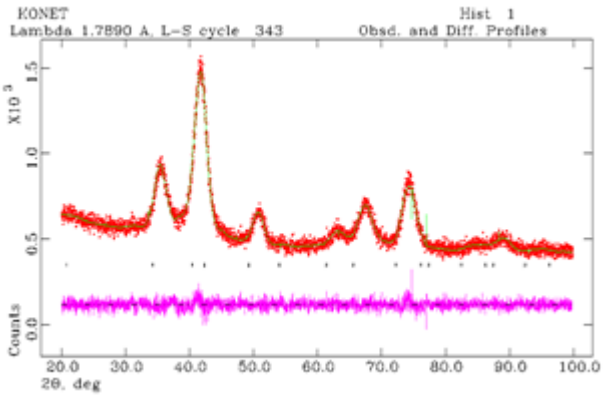

Figure 11. X-ray diffraction pattern of KONET.

The result of Rievelt Refinement Analysis
Crystall Lattice Parmeter
a = 8.5092(1) Å, b = 8.5092(1) Å c = 8.5092(1) Å,
α = β = γ = 90° = 90°, V = 616.1(3) Å^3 ρ = 3. 221 gr.cm^{-3}
Zn =0.4115,.Fe=2.5885
Non Stochiometri $Zn_{0.4115}Fe_{2.5885}O_4$

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 Rietvelt method of XRD analysis as follows;

a. Sample FISAC equation is $Zn_{0.409}Fe_{2.591}O_4$
Standat Enthalpi

b.Sample FISNET equation is $Zn_{0.416}Fe_{2.584}O_4$

$$H^0{}_{FISAC} = 0.409xH^0{}_{ZNO} + 0.591xH^0{}_{FeO} + 1xH^0{}_{Fe2O3}$$

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

$$\Delta H_{FISAC} = H^0_{ZF60} - H^{333}_{ZF60} = 5.69 - 2.696 = 2.994 \quad kcal/mol$$

$$S^0{}_{FISAC} = \left(\frac{2992}{333}\right) cal/\deg = 8.99\,[cal/\deg]$$

Standart Entalphi

$$H^0{}_{FISNET} = 0.416xH^0{}_{ZNO} + 0.584xH^0{}_{FeO} - 1xH^0{}_{Fe2O3}$$

$$= -11.19\,[kJoule/mole] = 11.19x0.239 = -2.68\ kcal/mole$$

$$\Delta H = 5.69 - 2.68 = 3.01$$

$$S^0{}_{FISNE} = \left(\frac{3001}{343}\right) = 8.64\,[cal/\deg]$$

Sample KONET equation is $Zn_{0.412}Fe_{2.588}O_4$
standard enthalpy

$$H^0{}_{Konet} = 0.412xH^0{}_{ZNO} + 0.584xH^0{}_{FeO} + 1xH^0{}_{Fe2O3}$$

$$= -11.272 \quad [kJoule/mole] = -2.69\ kcal/mole$$

$$\Delta H = H^{298}_{ZF} - H^0_{ZF} = 5.69 - 2.69 = 3.00$$

$$S^0{}_{Konet} = \left(\frac{3000}{333}\right) = 8.50\,[cal/\deg]$$

accordig with Edgar. F research [12] comparatif of the average of the zinc ferrite standart enthalpy ($H^0{}_{ZF}$) to the enthalpy of ZnFerrite at 298^{0}K ($H^{298}{}_{ZF}$) is 5690.9 cal/mol. There for the energy forming or activation of crystallization energy ΔS= *8.71 cal/deg* energy and entropy of the Zinc Ferrite.

Table 7. The comparative study of the crystallization activation

Method	Sample Type	Energy [kcal/mole]	Entropi [cal/mol Deg]
Isothermal	non Treat	4.27	12.2
NonIsothermal	non Treat	5.61	16.2
XRD analysis	Heat Treat	2.99	8.7
Avrage		4.29	12.37

Time of the synthesis process as the core of the Zinc-Ferrite successfully recorded graphed sigmoid of each temperature process in order to obtain specific energy formation process Zn Ferrite (FISAC, FISNET and KONET) is determined by the Arrhenius equation average a Qe = -1744.9 x 8314 = -14 507 joule / mol = -3.47 kcal / mol. Entropy at the temperature of 333 K = -10.4 [cal.mol-1 K-1]. The Salt solution at the reaction process Zn 2+, Fe 2+ and Fe 3+ with the alkaline solution of NaOH is exothermic.

The temperature effect of in the synthesis of the Zinc-Ferrite is limited below 90 ^{0}C do not give a significant difference to the material phase. The formation of the inversion index of the material formed of the Zinc-Ferrite worth almost the same. The difference in this thermodinamic analysis due to among 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.[15,16]

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 have to be examined carefully . The rate of change of temperature at any time due to different temperature to peak temperature of different of a minute of span the peak temperature when acquires.[16] .

The particle size of Zinc Ferrite can be maintained without agglomeration effect after synthesis in form of mud where each of the Zinc Ferrite particle coat by surface active substance.[17] According with thermodynamic analysis, the enthalpies formation of the Zinc ferrite 2-3 spinels around -2 till – 5 [kcal/mole] [18,19], 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.[17]. At 60, 70, and 80, Zn-Ferrite material is formed by co-precipitation method, it can mean that the doped Zn atoms in the compound became Zn Fe3O4 superparamagnetic Fe2O4 as a compound which is Excellent [20].

The Avrami-Ozawa equation originally has Logarithmic linear relationship between temperature changes have Logarithmic correlation R = 0.999 [21] relatively perfect. In this research, the level of correlation R = 0.85, which illustrates that the data obtained in this study still needs improvement. especially with regard to heat transfer occurs in both the FIS reactor isothermal and non-isothermal. The Westrum and Grimes (1957) has succeeded in making a linear relationship between standard entropy S against mass density of Zn Ferrite as figure 12 below, [22].

The average Zn Ferrite materials have activation energy of 4.2 kcal / mol with entropy rate of 12 cal / mol deg. Process methods which produces an average thermodynamic properties is an isothermal method. XRD analysis results show the value of the material density average Zn Ferrite 3:14 gm / cc, with the help of chart obtained the entropy value of about 13.cal/mol deg.

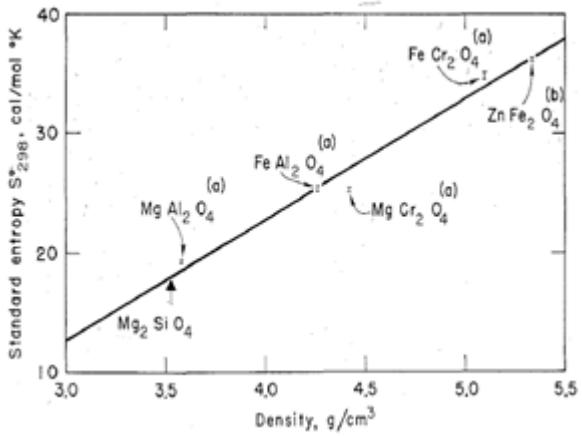

Figure 12. the graph of Density-Standart entropy correlation for normal spinel (a) Kelley King (1961)(b) Westrum and Grimes (1957) [22].

The X-Ray Diffraction analysis results show the value of the material density average Zn Ferrite 3:14 gm / cc, with the help of graphs obtained the entropy value of about 13.

IV. Conclusion

There is a difference between the the entropy the entropy calculation results with expected results chart on the method of X-ray diffraction considering yield heat-treated before the diffraction test due to heating could produce hollow cavity of a powder, it produces powder density decreasing the entropy yield non-isothermal process is relatively higher than the isothermal process, it indicates that the yield is more volatile than the yield of isothermal.

Events of occur during the heating treatment process to powder of yield , leading to a decline density , among other: releasing of free water (H2O) and bound (OH) lasts about 100oC to 300 ^{o}C.lease of gases, such as CO2 lasts about a temperature of 600 ^{0}C and at this stage accompanied by a reduction in material density.

Generally Zn Ferrite material can be processed using FIS techniques, with an activation energy of about 4:29 kcal / mol and entropy level around 12:4 cal / mol deg.

Although able 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.

Zn Ferrite material can be prepared by co-precipitation method. A practical way of implementing the process is capable both Installation of the injector made into the digester reactor it is to prevent the dwelling time particle growth process. According of the co-precipitate of yield, it is more universal with less interferences from coexisting constituents. However, the adaptation of co-precipitation procedures in the FIS reactor systems was rather late [24].

powder particles have a surface energy level lower than the surface energy yield in liquid form then proof that Zn Ferrite particles are on the yield of liquid is a nano particle.

The ZnFerrite particle behavior indirectly can be seen from Table 4, the results of Avrami estimation. FIS gave isothermal Avrami parameter n =0.578 and k =0.12, FIS non-isothermal Avrami parameter n =0.13 and k =0.17, it means having analogy with the kinetic analysis of the crystallization process in which the polymer material necessary process of complementation between the non-isothermal crystallization with isothermal crystallization [21,25]

i. The yield in the form of mud have some kind of binding energy as connective energy between solid particles with liquid, the surface energy of nano particles is greater than the surface energy of the bulky particles [23].

ii. The results of XRD measurement with helping by Rieldvelt refinement, the sistem is a measurement of the X-ray diffraction test is required to verify the portion of atoms that construct compound Zn Ferrite

Regarding the difference in the activation energy yield forecasts in the form of mud or ferrofuid with a yield in the form of powder can be described as follows; of recording events quickly with the proper coordination of the preparation can be done by using Flow Injection Synthesis. It is important to be able to follow the very fast reaction process so that it can perform parameter process tracing and application of generally Avrami equation to get a more detailed overview the physical characteristics and chemical properties of materials.

In this study was obtained the thermal properties of materials obtained Zn Ferrite formation at the low temperatures between 60 to 80 degrees, with the formation enthalpy (ΔH) 4.2 kcal / mol , entropy (S) 12.6 cal / mol deg and 3:14 density gr / cc, which is the contribution assessment basis of the isothermal and non-isothermal reaction then using Flow Injection Synthesis reactors , the thermodynamic parameters of materials forming reaction can be obtained in detail so the general Avrami equation can be used in their entirety.

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