Contents lists available at ScienceDirect



Arabian Journal of Chemistry



journal homepage: www.ksu.edu.sa

Kinetic formation of iron oxide nanoparticles using un- and γ -irradiated singular molecular precursor of Tris(pentanedionato)iron(III) complex

Asma A. Alothman

Department of Chemistry, College of Science, King Saud University, P.O. Box 22452, Riyadh 114935, Saudi Arabia

ARTICLE INFO ABSTRACT Keywords: Iron oxide nanoparticles were synthesized from tris(pentanedionato)iron(III) singular molecular precursor Iron Oxide Nanoparticles through pyrolysis in static air. FT-IR, XRD, TGA, BET and SEM/EDS techniques were used to follow the reactions Tris(pentanedionato)iron(III) and identify the products. Single crystalline iron oxide sizes were found to be $18.23 \pm 0.23, 16.42 \pm 0.21,$ and Singular Molecular Precursor 13.964 ± 0.11 nm using Scherrer equation, and the BET surface area were measured to be 110.909, 121.352, and Kinetic Formation 153.9911 m^2g^{-1} for the corresponding iron oxides obtained through pyrolysis of un-irradiated and γ irradiated tris(2,4 pentanedionato)iron(III) with 100 and 300 kGy, respectively. Nonisothermal kinetics formation of iron oxide nanoparticles over the thermal decomposition of un-irradiated and y-irradiated tris(pentanedionato)iron (III) molecular precursor with 100 and 300 kGy total γ -ray doses were investigated under air flow with a heating rate of 5, 10, 15, 20, and 25 °C/min, from 25 °C to 500 °C. Kinetic parameters were attained through modelfitting and model-free approaches, and artificial isokinetic relationship (IKR) for multi-step processes. The decomposition for both un-irradiated and γ -irradiated tris(pentanedionato)iron(III) molecular precursor with 100 and 300 kGy total y-ray doses proceed over one major step with two-dimensional diffusion (bi-dimensional particle shape) Valensi equation (D2).

1. Introduction

Magnetite, iron (II,III) oxide, is one of the well characterized naturally existence inorganic compound with the formula Fe₃O₄. It has a cubic inverse spinel structure contain a cubic close packed array of oxide ions and the Fe^{2+} ions fill half of the octahedral sites and the Fe^{3+} divided evenly and fill the tetrahedral and the remaining other half octahedral sites.(Cornell & Schwertmann, 2003; Pereira et al., 2012; Wu et al., 2021) Due its structure and related chemical, electrical, and magnetic properties besides to its low toxicity, cost effective, stability it has enormous number technological applications in deferent fields including but not limited in medicine, data storage device, catalysis, and environmental remediation.(Ajinkya et al., 2020; Al-Anazi, 2022; Israel et al., 2020; Teja & Koh, 2009; Xu et al., 2012) Despite the various chemical approaches employed to Magnetite iron oxide, there remain challenges related to suboptimal quality, unclear morphology, prolonged synthesis times, and high-temperature requirements. To address these issues, a more favourable synthesis approach such as coprecipitation (Petcharoen & Sirivat, 2012; Valenzuela et al., 2009), solvothermal (Bastami et al., 2012; Bastami et al., 2014), hydrothermal (Kumar et al., 2020; Torres-Gómez et al., 2019) and others are sought. Among these techniques, the electrochemical method stands out as it allows for the rapid formation of iron oxide nanoparticles at ambient temperature. However, the disadvantages of sonoelectrochemical synthesis include limited control, leading to variations in product quality and consistency, operational costs, equipment complexity, limited scalability for industrial applications due to equipment constraints and energy requirements, and environmental impact such as noise pollution, the disposal of related waste materials can pose environmental concerns, and sonochemical reactions can sometimes lead to unwanted side reactions or byproducts, reducing the selectivity of the synthesis process (Dudchenko et al., 2022). The high-temperature pyrolysis method provides distinct advantages in iron oxide nanoparticle synthesis compared to the cost-effective sonoelectrochemical approach. Pyrolysis allows for precise control over particle size and crystallinity, ensuring consistent, high-quality results, while sonoelectrochemical methods may yield less predictable outcomes due to their limited control, making pyrolysis a preferred choice for precise and reliable nanoparticle production. It has been established that the iron oxide particles size, sizes distribution, shapes, and surface nature impact the magnetic properties of iron oxide nanoparticles.(Carvalho et al., 2013; Filippousi et al., 2014; Ibarra-Sánchez et al., 2013; Muro-Cruces et al., 2019; Ngoi et al., 2021; Roca

Peer review under responsibility of King Saud University. Production and hosting by Elsevier.

https://doi.org/10.1016/j.arabjc.2023.105531

Received 22 July 2023; Accepted 4 December 2023 Available online 6 December 2023

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Fig. 1. FTIR spectra of un-irradiated and γ irradiated tris(2,4-pentanedionato)iron(III) with 100 and 300 KGy, respectively.

et al., 2019) One widely used way to control physicochemical properties such as particles sizes and size distribution is to produce magnetic nanoparticles by a high-temperature decomposition treatment of singular inorganic molecular precursor.(Belaïd et al., 2018; Maity et al., 2009: Miguel-Sancho et al., 2012: Roca et al., 2019: Roca et al., 2006: Siddigi et al., 2007; Toyos-Rodríguez et al., 2019) On the other effective used way, the gamma Co-60 ray irradiation is desirable for producing controlled size nanoparticles in large scale with clean process.(Choi et al., 2005; Flores-Rojas et al., 2020; Jurkin et al., 2016; Marić et al., 2020; Nguyen et al., 2019; Remita et al., 1996) Although there are many studies have investigated the role of γ -irradiation on the thermal decomposition of inorganic precursor, the kinetics of the decomposition of the un- and γ -irradiated singular molecular precursor of tris(pentanedionato)iron(III) complex to obtain iron oxide nanoparticles have been considered less. Thermogravimetry analysis technique (TGA) is very valuable method particularly for exploring the decomposition reactions mechanism and its kinetics.(Laye et al., 2007). The influence of gamma irradiation on the weight loss behavior observed in the Thermogravimetric Analysis (TGA) curve of an inorganic complex is a pivotal aspect, offering profound insights into the material's thermal stability and decomposition characteristics. TGA, a method tracking weight changes in response to controlled temperature variations, becomes a potent tool to discern alterations induced by gamma irradiation in the molecular structure and properties of the inorganic complex. Thus herein, the main objective of the research is to investigate the impact of γ -irradiation on the structure of the singular molecular precursor tris (pentanedionato)iron(III) complex and its subsequent influence on the structure and morphology of iron oxide nanoparticles. Iron oxide nanoparticles were synthesized through pyrolysis of both unirradiated and y-irradiated singular molecular precursors at different temperatures. The kinetics of the thermal decomposition of unirradiated and γ -irradiated tris(pentanedionato) iron(III) samples were also assessed and compared. Both model-fitting and isoconversional methods were employed to examine the reliability of each model category in

describing the pyrolysis kinetics of unirradiated and γ -irradiated tris (pentanedionato) iron(III) samples, aiming to produce iron oxide nanoparticles. We elucidate the decomposition reaction mechanism of the tris(pentanedionato)iron(III) complex and its kinetics using thermal kinetic analysis, which appears to proceed through a two-dimensional diffusion process (bi-dimensional particle shape) described by the Valensi equation (D₂). This suggests that stable nuclei form at a slower rate than their subsequent growth. Our results highlight the significant influence of pyrolysis temperature and absorbed dose on controlling the structure and morphology of iron oxide nanoparticles.

2. Experimental

Powder of tris(2,4-pentanedionato)iron(III)-Fe(C₅H₇O₂)₃ > 98 % was obtained commercially from TCI and were used without any further purification. The irradiation process involved compressing tris(2,4pentanedionato)iron(III) samples in glass vials under vacuum, followed by γ -irradiation at a dose rate of approximately 26 kGy/h with constant intensity, utilizing a Co-60 Gamma cell 220 (Nordion MDS, Ontario, Canada). The absorbed doses administered were 100 and 300 kGy. Calibration of the radiation source was performed using a Fricke ferrous sulfate dosimeter for comparison. Dose calculations involved adjustments to the photon mass attenuation and energy-absorption coefficient for both the sample and the dosimeter solution. These corrections were meticulously applied to ensure the accuracy of the computed doses (Spinks & Woods, 1990). Tris(2,4-pentanedionato)iron(III) samples were calcined at 180, 200, 220, 240, 260, and 280 °C for 6 h each. The un-calcined and calcined samples before and after irradiations were characterized through recording the FTIR spectra in the range of 4000–400 cm^{-1} as KBr pellets with of a concentration of 1 % using a Perkin-Elmer FT-IR spectrometer, and collecting XRD patterns at the diffraction angles range of 5° to 100° utilizing Bruker (model D8 ADVANCE) X-ray diffractometer with a nickel filter and Cu Ka radiation ($\lambda = 1.5406$ Å[°] at 40 kV and 40 mA). The thermal decomposition

Table 1

FTIR bands of un-irradiated and irradiated tris(2,4-pentanedionato)iron(III) samples and their assignments.

	Frequency (cm^{-1})					
band assignment*	un- irradiated	γ- irradiated (100 kGy)	γ- irradiated (300 kGy)			
ν(OH)	3429	3429	3428			
$\nu_{a}(CH_{3})$ in plane	3005	3005	3005			
$\nu_a(CH_3)$ out of plane	2961	2962	2962			
$\nu(OH) + \nu_s(CH_3)$	2919	2919	2920			
ν_a (C–C–C-O) + δ (OH) + ν (C-O)	1571	1571	1571			
ν (C–C) + δ (OH)	1525	1525	1525			
$ \begin{split} &\delta_a(CH_3) \text{ in plane} + \delta_s(CH_3) \text{ out of} \\ & \text{plane} + \nu_a(C\text{-}C\text{-}C\text{-}O) + \delta(OH) \\ & + \delta(CH) + \nu(C\text{-}CH_3) \end{split} $	1426	1426	1426			
$\delta_{s}(CH_{3})$	1361	1361	1361			
$ u_{s}$ (C–C–C-O) + ν (C-O) + δ (OH) + ν (C-CH ₃)	1271	1271	1271			
δ (C–H) olefinic + π (CH ₃) + γ (OH)	1188	1188	1188			
π (CH ₃) + ρ (CH ₃) + γ (OH) + τ (C-C-C-H) + τ (O-C-C-H)	1017	1017	1017			
ρ (CH ₃) + γ (OH) + ν (C-O) + ν (Fe-O-C)	927	927	927			
ρ(C–H)	799	799	799			
γ(C–H) olefinic	770	770	770			
$\label{eq:gamma-field} \begin{split} \Gamma \mbox{ ring } + \rho(\mbox{CH}_3) + \tau(\mbox{C-C-H}) + \\ \tau(\mbox{O-C-C-H}) \end{split}$	664	664	664			
$\Delta \operatorname{ring} + \pi(\operatorname{CH}_3) + \nu(\operatorname{Fe-O}) + \gamma(\operatorname{Fe-O}) + \delta(\operatorname{O-C-C})$	552	552	552			
$ u$ (Fe-O) + δ (O-Fe-O) + Δ ring + δ (C-CH ₃)	433	433	434			
* ν , stretching; δ , in plane bending; γ , out of plane bending; π , CH ₃ out of plane rocking;						

ρ, CH₃ in plane rocking; Δ, in plane ring deformation; Γ, out of plane ring deformation; τ, torsion; s, symmetric; a, asymmetric.

deformation, 1, torsion, s, symmetric, a, asymmetric

analysis of tris(2,4-pentanedionato)iron(III)-samples before and after radiation were carried using Perkin–Elmer (dynamic) thermogravimetric techniques. The kinetic analysis was calculated from temperature measurements made during the actual period of a material

decomposition employing model-fitting and model-free methods to produce consistent kinetic characteristics from nonisothermal experiments in which the instrument was programmed to heat the sample from 25 °C to 500 °C at a constant heating rate of 5, 10, 15, 20, and 25 °C/min under air flow. Surface area and pore size of samples were measured via automated gas sorption analyser (Quantachrome Instruments) using N2 adsorption/desorption isotherms. Samples were initially outgassed at 60 °C for 60 min under vacuum to a final pressure of 0.35 Pa and then the data obtained over the relative pressure range of $(P/P^{\circ} =$ 0.05-0.99). The data were calculated based on Brunauer-Emmett-Teller (BET) equation, Langmuir models Barrett-Joyner-Halenda (BJH). Samples morphology and surface composition were acquired utilizing Scanning Electron Microscopy (SEM/EDX, JEOL JSM-6380LA) using different magnification powers and operating between 5 and 20 kV. Samples were displayed on a carbon tube with coating with gold before being examined. chemical elements of the sample were determined using Elemental Analysis (EDX) at 20 kV.

3. Results and discussion

3.1. Characterization of iron oxide nanoparticles and γ - irradiation role in its formation

The role of irradiation on the characteristic FTIR bands of tris(2,4pentanedionato)iron(III) precursors were elucidated and shown in Fig. 1. As shown, the FTIR spectra of un-irradiated and γ -irradiated tris (2,4-pentanedionato)iron(III) with 100 and 300 kGy, respectively; in agreement with the literature (Slabzhennikov et al., 2003; Tayyari & Milani-nejad, 2000) displayed the characteristic bands assigned to various vibration modes of acetylacetonate functional groups with no disappearance or appearance of new bands as were recorded in the FTIR spectra of γ -irradiated tris(2,4-pentanedionato)iron(III) samples with 100 and 300 kGy total γ ray doses. However, a decrease in the intensity of most characteristic bands was recorded as results of γ -irradiation. The bands intensities designated to ν Fe-O bond in the range of 799 to 433



Fig. 2. XRD patterns (a) of un-irradiated and γ irradiated tris(2,4 pentanedionato)iron(III) with 100 and 300 kGy, respectively.



Fig. 3. SEM/EDS analysis of un-irradiated (a and d) and γ irradiated tris(2,4 pentanedionato)iron(III) with 100 (b and e) and 300 kGy (c and f), respectively.



Fig. 4. Effects of γ -ray on the thermal decomposition behaviour of tris(pentanedionato)iron(III) samples.

cm⁻¹ were more affected by irradiation than any other bands in the spectrum. The decreased in the intensity of this band could be attributed to bond divided or split influenced by γ irradiation.(Aly & Elembaby, 2020; El-Boraey et al., 2022) IR bands for tris(2,4-pentanedionato)iron (III) and their assignments are listed in Table 1.

The role of irradiation on the XRD patterns of tris(2,4-

pentanedionato)iron(III) precursors were also explored as shown in Fig. 2 which presented XRD patterns of un-irradiated and γ irradiated tris(2,4 pentanedionato)iron(III) with 100 and 300 kGy, respectively. The main peaks located at 10.99° (020), 13.27° (consisting of two superimposed peaks, 13.28° (002) and 13.26° (201)), 17.08° (022), 21.54° (321), 22.96° (203), 23.95° (232) and 25.43° (223) matching



Fig. 5. FT-IR spectra of un-irradiated tris(2,4-pentanedionato)iron(III) calcined at different temperatures for 6 h.



Fig. 6. FT-IR spectra of γ -irradiated tris(2,4-pentanedionato)iron(III) with 100 kGy radiation dose calcined at different temperatures for 6 h.

a reference primitive orthorhombic phase (ICCD Card No: 00–030-1763) (Dudek et al., 2020). XRD diffractograms proved that orthorhombic tris (2,4 pentanedionato)iron(III) was only dominated phase in unirradiated and γ irradiated samples and thus maintains its structural integrity after exposure to the irradiation dose. However, tris(2,4 pentanedionato)iron(III) exposure to the 300 kGy irradiation dose not only



Fig. 7. FT-IR spectra of γ -irradiated tris(2,4-pentanedionato)iron(III) with 300 kGy radiation dose calcined at different temperatures for 6 h.

resulting in broadening of the main peaks but also appears a loss of peak intensity in addition to the 020 peak 20 position specifically shift to 10.70° . This then demonstrates that irradiation doses with 300 kGy doses cause decreasing the degree of crystallinity and more damage to tris(2,4 pentanedionato)iron(III) than 100 kGy doses.

The irradiation effect on the morphology and surface elemental compositions of tris(2,4-pentanedionato)iron(III) precursors samples were examined as Fig. 3 displayed the effects of γ -ray on SEM images and EDS analysis of un-irradiated and γ irradiated tris(2,4 pentanedionato)iron(III) with 100 and 300 kGy samples. It can be clearly seen that the structure of inspected samples is ambiguous in nature, displaying a random size distribution for both un-irradiated and γ -irradiated samples containing of nearly spherical-shape nanoparticles that agglomerated together to form significant large grains that uniformly distributed throughout the matrix of the samples. The agglomeration of the grain crystallites increases with increasing the γ -irradiation with no discrete particles are noticeable in precursors samples. The EDS spectra revealed distinct signals at 0.25, 0.50, 0.57, and 6.40, corresponding to C, O, and Fe, respectively. Additionally, unassigned signals at 0.00 and 2.2 were identified, associated with C and Au, Tris(pentanedionato)iron(III) complexes exhibit minimal alterations when subjected to 100 and 300 kGy doses of gamma irradiation, as depicted in Fig. 4. Despite the application of high-energy photons inducing subtle changes evident in the resulting TGA curve, the complex remains remarkably stable. The intricate portrayal of the complex's thermal decomposition, leading to the formation of iron oxide and the subsequent release of byproducts, is clearly manifested in the TGA curve. The discernible impact of gamma irradiation on weight loss is characterized by slight shifts in the onset temperature of decomposition, fluctuations in the degradation rate, and modest alterations in the overall mass loss profile, reflecting the stability of the complex under the influence of gamma radiation. The TGA curves of un-irradiated tris(2,4 pentanedionato)iron(III) and γ -irradiated with 100 kGy displayed one major decomposition step with weight loss of 85.4 % in the range of 180 to 240 °C attributed to the thermolysis of pentanedionato moiety of the tris(2,4 pentanedionato)iron(III) phase resulting in the rapid formation of degradation products of gaseous residues and small iron oxide nuclei. The final weight of 14.6 % (calculated 21.8 %) is presumed to be the residue of the oxygen deficient iron oxide material. TGA curve demonstrates that γ -irradiated tris(2,4 pentanedionato)iron(III) with 100 kGy shows no apparent response to gamma irradiation doses and retains the thermolysis behaviour without any observed changes. Thermolysis of γ -irradiated tris(2,4 pentanedionato)iron(III) with 300 kGy rate dose exhibited similar behaviour with one major step with weight loss of 78.6 % in the range of 180 to 240 °C due to decomposition of pentanedionato moieties, and the final weight of 21.4 % (calculated 21.8 %) is presumed to be iron oxide products. The continuous weight loss on approaching 500 °C as consequence of decomposition of remaining carbonaceous species.

The un-irradiated and γ irradiated tris(2,4 pentanedionato)iron(III) with 100 and 300 kGy, were calcined at selected temperature of 180, 200, 220, 240, 260, and 280 °C for 6 h each. Figs. 5 to 7 show the temperature-dependent FTIR spectra of un- and y-irradiated calcined tris (2,4-pentanedionato)iron(III) with 100 and 300 kGy, respectively. The characteristic absorption bands of 2,4-pentanedionato gradually decrease with the increasing temperature and disappear when the temperature reaches 280 °C, which indicates completion of the decomposition of 2,4-pentanedionato residues. The observed FTIR bands in the range of 800—400 cm⁻¹, attributed to Fe-O vibrations, exhibit an intriguing behavior of increasing intensity with rising temperature. These bands are linked to the vibrational modes associated with specific iron oxide phases, and their variations at different temperatures provide valuable insights into the thermal evolution of the formed iron oxide. At 240 °C, the presence of bands at 660, 614, 550, 446, and 428 cm⁻¹ aligns with the characteristic vibrational modes of magnetite (Fe₃O₄). The increased intensity of these bands at higher temperatures may indicate enhanced crystallinity or phase transitions within the magnetite structure. Upon further heating to 260 °C, additional bands at 728, 692, 640, 560, 480, 444, and 428 $\rm cm^{-1}$ emerge.



Fig. 8. Temperature-dependent XRD patterns of the un-irradiated tris(2,4-pentanedionato)iron(III).



Fig. 9. XRD patterns of γ -irradiated tris(2,4-pentanedionato)iron(III) with 100 kGy radiation dose calcined products at different temperatures for 6 h.

These bands are associated with vibrational modes characteristic of maghemite (γ -Fe₂O₃). The growing intensity of these bands suggests a temperature-induced transformation towards maghemite, possibly indicating the conversion from magnetite to maghemite. At 280 °C, the

vibrational bands at 728, 697, 640, 560, 484, 444, and 424 $\rm cm^{-1}$ remain, affirming the persistence of maghemite characteristics. The variations in band intensity across temperatures imply dynamic phase changes and the influence of thermal treatment on the iron oxide



Fig. 10. XRD patterns of γ-irradiated tris(2,4-pentanedionato)iron(III) with 300 kGy radiation dose calcined products at different temperatures for 6 h.



Fig. 11. XRD patterns of the solid residues obtained from pyrolysis of un-irradiated and γ-irradiated tris(2,4-pentanedionato)iron(III) precursors with 100 and 300 kGy, respectively.

system. However, it's important to note that the identification of phases based on FTIR bands is indicative, and definitive confirmation often requires complementary techniques such as X-ray diffraction (XRD). The observed changes underscore the sensitivity of FTIR spectroscopy to alterations in the crystalline structure and phase composition of iron oxides under different thermal conditions (Stoia et al., 2016; Waldron,

Table 2

Crystallite Size, surface area, pore volume, and pore radius of iron oxide samples.

Iron oxide samples	Crystallite Size (nm)	Particle size(nm)	Surface area (m²/ g)	Pore volume (cm ³ /g)	Pore radius (Å)
un- irradiated	$\begin{array}{c} 18.23 \pm \\ 0.23 \end{array}$	$\begin{array}{c} \textbf{28.65} \pm \\ \textbf{4.08} \end{array}$	110.909	0.236	37.651
irradiated (100 kGy)	$\begin{array}{c} \textbf{16.42} \pm \\ \textbf{0.21} \end{array}$	$\begin{array}{c} \textbf{27.35} \pm \\ \textbf{6.14} \end{array}$	121.352	0.310	23.152
irradiated (300 kGy)	$\begin{array}{c} 13.964 \pm \\ 0.11 \end{array}$	$\begin{array}{c} \textbf{22.99} \pm \\ \textbf{4.46} \end{array}$	153.991	0.361	23.294

1955; Yadav et al., 2020). Moreover, the observed broad band at 3401 cm⁻¹ and band at 1624 cm⁻¹ were attributed to both symmetrical and unsymmetrical modes of O–H bonds of adsorbed water layer associated to the surface iron atoms. The temperature-dependent FTIR spectra of γ -irradiated calcined tris(2,4-pentanedionato)iron(III) with 100 and 300 kGy as seen in demonstrated similar behaviour with decreasing intensities of the iron oxide characteristic absorption bands for the calcined sample of tris(2,4-pentanedionato)iron(III) precursor with 300 kGy sample related to the calcined un-irradiated sample of tris(2,4-

pentanedionato)iron(III) precursor.

Figs. 8-10 show the temperature-dependent XRD patterns of un- and γ -irradiated calcined tris(2,4-pentanedionato)iron(III) with 100 and 300 kGy, respectively. Through calcination at 180, 200, 220, 240, 260, and 280 °C for 6 h each, an immediate structural loss of the corresponding tris(2,4-pentanedionato)iron(III) precursor was observed accompanied by the emission of carbonous gases from 2,4-pentanedionato moieties decomposition resulting in the formation of amorphous phases contain iron oxide. Moreover, the reflection signal located at 2θ of 36° in the diffractogram of calcined sample at 220 °C started to appear signalling the formation of iron oxide material phase. Upon increasing of calcination temperatures reaching 280 °C as shown in Fig. 11, All the reflections in the XRD patterns can be indexed to Magnetite iron oxide phase (ICCD Card No: 00-003-0863). The characteristic peaks at 30.4°, 35.8°, 43.5°, 53.9°, 57.4°, and 63.2° match to the (220), (311), (400), (422), (511), and (440) crystal faces of Fe₃O₄, respectively. The signals get well defined and narrowed indicating the effect of pyrolysis temperatures on the XRD patterns in alignment with the FTIR and TGA analyses conforming of nanocrystalline iron oxide phase developments. The peaks are found at 12.77° can be attributed to the amorphous phase of carbon or to deletion of some specific interlayered atoms leads to increased intensities.(Sun et al., 2017) The crystallite size of the



Fig. 12. SEM image, particle size distribution histogram, and EDS analysis of un-irradiated (a, d and g) and γ irradiated of the solid residues obtained from pyrolysis of tris(2,4-pentanedionato)iron(III) precursors with 100 (b, e and h) and 300 kGy (c, f and i), respectively.

0.00



Fig. 13. α -T (K) curves of the thermal decomposition for (a) un-irradiated, (b) γ -irradiated with 100 kGy radiation dose, and (c) γ -irradiated with 300 kGy radiation dose of tris(pentanedionato) iron (III) samples in static air at different heating rates.

prepared iron oxide samples was calculated by averaging the values obtained from the (220), (311), (400), (422), (511), and (440) diffraction peaks, utilizing the Debye-Scherrer equation (Eq. (1):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

Where, D is the diameter of crystalline size, λ is the wavelength of the incident beam, β is the full width half maxim 'FWHM', and θ is the Bragg's angle. The crystallite size as Table 2 demonstrated represents the size of the individual crystalline domains within the nanoparticles. In the un-irradiated sample of iron oxide samples obtained from pyrolysis, the crystallite size is 18.23 \pm 0.23 nm, which decreases to 16.42 \pm 0.21 nm and 13.964 \pm 0.11 nm for the 200 kGy and 300 kGy irradiated samples, respectively. The reduction in crystallite size with increased irradiation suggests a transformation in the crystal structure, potentially due to radiation-induced defects or phase changes. Fig. 12 clearly indicated that the as-prepared iron oxide materials were nearly spherical-shape nanoparticles with average size of 28.65 ± 4.08 , 27.35 \pm 6.14, and 22.99 \pm 4.46 nm for samples obtained from pyrolysis of unirradiated and γ -irradiated tris(2,4-pentanedionato)iron(III) precursors with 100 and 300 kGy, respectively (Table 2). The particles agglomerated together, and elements distributed uniformly all over the matrix of the samples. These results confirmed that the corresponding oxides kept the spherical morphology with a broader size distribution of the apparent original precursors. The agglomeration of the grain crystallites increases, and the particle size decreases with increasing the y-irradiation. Pore size and BET surface area are vital indicators of the nanoparticles' structural characteristics (Figure S4 in SF Text). In the un-

irradiated sample, the pore radius is 37.651 Å, while the BET surface area is 110.909 m^2/g . With irradiation, the pore radius decreases to 23.152 Å (200 kGy) and 23.294 Å (300 kGy), and the BET surface area increases to $121.352 \text{ m}^2/\text{g}$ (200 kGy) and $153.991 \text{ m}^2/\text{g}$ (300 kGy). The reduction in pore radius and increase in BET surface area suggest enhanced porosity and surface reactivity, possibly attributable to the radiation-induced structural modifications. The dynamic changes in crystallite size, pore size, and BET surface area highlight the influence of irradiation on the physical properties of the nanoparticles. These alterations are pivotal for tailoring nanoparticles to potential specific applications, whether in catalysis, sensing, or drug delivery, and underscore the importance of a comprehensive understanding of their evolving characteristics under different irradiation conditions. Fig. 12 also demonstrate the EDS analysis of un-irradiated and γ irradiated of the solid residues obtained from pyrolysis of tris(2,4-pentanedionato) iron(III) precursors with 100 and 300 kGy, respectively. The unirradiated sample showcases weight percentages of 33.43 % oxygen (O) and 66.57 % iron (Fe). The calculated Fe/O ratio approximates 2. indicating a molecular formula close to O₂Fe₁. This aligns with the expected composition of iron oxide, potentially magnetite, emphasizing the dominant role of iron in the molecular structure. Upon irradiation with 100 kGy, a shift in weight percentages to 30.87 % O and 69.13 % Fe alters the Fe/O ratio to approximately 2.24, suggesting a modified molecular formula of O_{1.9}Fe_{1.2}. The increased iron content implies potential phase transformations induced by irradiation, influencing the material's composition. At 300 kGy, weight percentages further change to 23.71 % O and 76.29 % Fe. The Fe/O ratio increases to about 3.21, indicating a shift towards O1.4 Fe1.3. This substantial alteration suggests



Fig. 14. Kinetic analysis of α/T (K) curves of the thermal decomposition of tris(pentanedionato) iron (III) samples according to CR (top) and CK (bottom) for (a and d) un-irradiated, (b and e) γ -irradiated with 100 kGy, and (c and f) γ -irradiated with 300 kGy radiation dose.

a more pronounced impact of irradiation, potentially leading to the formation of iron-rich phases. The observed trends in molecular formulas and Fe/O ratios imply a dynamic response to radiation. The increasing Fe/O ratio suggests progressive iron enrichment, possibly indicating the formation of iron oxides with higher irradiation doses. Acknowledging the simplified nature of these estimations, further characterization techniques like Mössbauer spectroscopy are essential for precise phase identification. Overall, the EDS data illuminates the evolving molecular composition and Fe/O ratios, offering valuable in-sights into irradiation's impact on the material's structure and potential phase transformations.

3.2. Kinetic Studies

The solid-state decomposition reactions of tris(pentanedionato) iron (III) can be depicted through with a single-step kinetic equation according to Eq. (2).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

Where $\frac{d\alpha}{dt}$ is the reaction rate, $t (\min^{-1})$ is the time, k(T) is the rate constant depending on temperature, T(K) is the absolute temperature, $f(\alpha)$ is the reaction model, and α is the degree of conversion which calculated via $\alpha = \frac{m_0 - m_0}{m_0 - m_\infty}$; m_0 (mg) is the initial weight of the sample, m (mg) is the weight of the sample at temperature T, and m_∞ (mg) is the final weight of the sample. (Galwey & Brown, 1998; Reading, 1998; Sharp et al., 1966; van Ekeren, 1998). The Arrhenius equation is applied to explicitly integrate the temperature dependence into the rate constant (Eq. (3):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp(-\frac{E_a}{RT})f(\alpha) \tag{3}$$

In this expression, A represents the pre-exponential factor (min^{-1}) ,

 E_a is the activation energy (kJmol⁻¹), and *R* signifies the gas constant. The amalgamation of Arrhenius parameters and the reaction model is commonly referred to as the kinetic triplet (E_a , *A*, and f(a)). In situations involving nonisothermal conditions, where a sample undergoes constant-rate heating, the explicit temporal dependence in Eq. (3) is eliminated through a straightforward transformation (Eq. (4):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \exp(-\frac{E_a}{RT}) f(\alpha) \tag{4}$$

Here, $\frac{dt}{dt} = \beta$ denotes the heating rate. Fig. 13 examines the influence of heating rate on the thermal decomposition of un- and γ -irradiated tris (pentanedionato) iron (III) samples materials. Fig. 13 illustrates that higher heating rates shift the reaction zone towards elevated temperatures. This phenomenon results from the varied residence times of tris (pentanedionato) iron (III) samples under different heating rates. The relationship between heating rates and residence time is inversely proportional; lower heating rates correspond to longer residence times, allowing thermal gradients to penetrate the inner core of sample particles. The kinetic triplet parameters for each decomposition step can be derived by rearranging and integrating the non-isothermal rate law from Eqs. (4) and (5), employing both model-fitting and isoconversional approximations.

$$g(\alpha) = \frac{AE_a}{\beta R} P(x) = \frac{A}{\beta} I(E_a, T)$$
(5)

Where $P(x) = \int_0^{\alpha} [f(\alpha)]^{-1} d\alpha$ is the exponential integral which has numerous approximations and no direct analytical solution. (Brown, 1997; Galwey & Brown, 2000; Khawam & Flanagan, 2005; Vyazovkin, 2000).

3.2.1. Model-fitting approaches

The solid-state reaction model equations, **Table A in SF Text**, employed into experimental data to obtain the kinetic parameters



Fig. 15. Kinetic analysis of the thermal decomposition of tris(pentanedionato)iron (III) samples according to KAS (top), T (middle), and FWO (bottom) for (a, d, and g) un-irradiated, (b, e, and h) γ-irradiated with 100 kGy, and (c, f, and i) γ-irradiated with 300 kGy radiation dose.

through model-fitting approaches using Coates and Redfern (CR) and Clark and Kennedy (CK) model displayed in Eqs. (6) and (7). (Coats & Redfern, 1964; Kennedy & Clark, 1997; Vyazovkin, 2000; Vyazovkin & Wight, 1999a)

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E_a} \left[1 - \left(\frac{2RT^*}{\beta E_a}\right)\right]\right) - \frac{E_a}{RT}$$
(6)

$$\ln\frac{\beta g(\alpha)}{T-T^{\circ}} = \ln A - \frac{E_a}{RT}$$
(7)

Where T^* and T^r is the mean and initial temperatures, respectively. Kinetic parameters for un-irradiated and γ -irradiated tris(2,4-pentanedionato)iron(III) with 100 and 300 kGy are obtained by plotting the left-hand side of both equations versus the inverted temperatures. (Rodante et al., 2002) From the slope and intercept of CR and CK equations the values of E_a , A, and r were obtained (**Tables B to G in SF Text**). The function model with best linear of temperature dependency to evaluate the reaction rate constant k(T) found to be adapting the two-dimensional diffusion (bi-dimensional particle shape) Valensi equation (D₂) as shown in Fig. 14 for all samples.

3.2.2. Isoconversional approaches

In nonisothermal experiments, the difficulty lies in distinguishing temperature dependence k(T) from the reaction model f(a), resulting in uncertainties in Arrhenius parameters that compensate for disparities between assumed and actual reaction models. Model-fitting provides a single, averaged activation energy, overlooking variations with temperature and conversion extent. Isoconversional methods address these

challenges by determining activation energy without assuming the reaction model, thereby providing more consistent kinetic results across experiments. (Vyazovkin & Wight, 1999b) Isoconversional approaches were utilized to estimate the relation between activation energy (E_a) and the degree of conversion (α) on dependency of the temperature (T) based on model-free assumptions. (Khawam & Flanagan, 2005; Sbirrazzuoli & Vyazovkin, 2002) Several approaches, include Kissinger-Akahira-Sunose (KAS), Tang (T), and Flynn-Wall-Ozawa (FWO) equations as Eqs. (8)–(10) demonstrated (Flynn & Wall, 1966; Kissinger, 1957; Tang & Chaudhri, 1980), were employed by plotting the left-hand sides against the inverted temperatures which gave a straight line at each value of α as Fig. 15 illustrated, and from the slope and intercept of each lines the activation energy were deduced (**Table H in SF Text**).

$$\ln\beta = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.3305 - 1.052\left(\frac{E_a}{RT}\right)$$
(8)

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\frac{AR}{E_a g(\alpha)} - \frac{E_a}{RT}$$
(9)

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = \ln\left[\frac{AE_a}{Rg(\alpha)}\right] + 3.635041 - 1.894661\ln E_a - 1.001450 \frac{E_a}{RT}$$
(10)

Further, Vyazovkin (VYZ) isoconversional approximation with 5th degree Senum-Yang approximation (Eqs. (11) and (12) was used by Gorbachev (Eq. (13), Agrwal (Eq. (14), and Sivaubramanin-Cai (Eq. (15) integrations to determine the apparent activation energy ($E_{a,a}$) at any specific value of the extent of the conversion (α) in which the value of Ω



Fig. 16. The activation energy plotted as a function of the extent of the conversion for (a) un-irradiated, (b) γ-irradiated with 100 kGy, and (c) γ-irradiated with 300 kGy radiation doses.

is minimized.(Saha & Ghoshal, 2006; Saha et al., 2006; Vyazovkin, 2000; Vyazovkin & Wight, 1997, 1999a) Fig. 16 displays similar dependency of $E_{a,\alpha}$ as a function of α using different isoconversional approximations for un-irradiated and γ -irradiated with 100 and 300 kGy radiation doses. Moreover, the $E_{a,\alpha}$ values of γ -irradiated tris(pentanedionato)iron(III) with 100 and 300 kGy radiation doses were increased in comparison to un-irradiated sample could be relay on reduction of active nucleation sites as role of irradiation during the decomposition reaction. The process assumed to be single step initially started with

increasing activation energy with increasing the extant of conversion due to decomposition of organic residues and the formation of active nucleation centres of iron oxide. Furthermore, the $E_{a,a}$ values differences attributed to temperature integral approximations that were used in base-relations derivations of KAS, T, FWO, VAS equations.

$$\Omega = \left| \sum_{i=1}^{n} \sum_{i\neq j}^{n} \frac{I(E_{a,a}, T_{a,i})\beta_j}{I(E_{a,a}, T_{a,j})\beta_i} \right|$$
(11)



Fig. 17. The isokinetic relationships obtain by CR and CK methods for unirradiated and γ - irradiated tris(pentanedionato)iron(III) samples.

 Table 3

 Artificial isokinetic parameter obtained by CR and CK methods.

Method	$a(\min^{-1})$	b(mol KJ ⁻¹)	k _{iso} (min ⁻¹)	T_{iso} (K)	r ²
CR (un-irradiated)	-12.4080	0.2315	4.09 × 10 ⁻⁶	519.5639	0.9966
CR (γ-irradiated (100 kGy))	-12.4020	0.2298	4.11 × 10 ⁻⁶	523.4075	0.9959
CR (γ-irradiated (300 kGy))	-11.9180	0.2265	6.67 × 10 ⁻⁶	531.0333	0.9957
CK (un-irradiated)	-2.7136	0.2307	6.63 × 10 ⁻²	521.3656	0.9962
CK (γ-irradiated (100 kGy))	-2.5951	0.2287	7.46 × 10 ⁻²	525.9250	0.9965
CK (γ-irradiated (300 kGy))	-2.6055	0.2287	7.39×10^{-2}	525.9250	0.9965

$$I(E_{a,\alpha},T_{\alpha}) = \int_{0}^{T_{\alpha i}} \exp\left(\frac{-E_{a,\alpha}}{RT}\right) \mathrm{d}T$$
(12)

$$\int_{0}^{T} \exp\left(\frac{-E_{a}}{RT_{ai}}\right) \mathrm{d}T = \frac{RT_{ai}^{2}}{E_{a}} \left(\frac{1}{1 + \frac{2RT}{E_{a}}}\right) \exp\left(\frac{-E_{a}}{RT_{ai}}\right)$$
(13)

$$\int_{0}^{T} \exp\left(\frac{-E_{a}}{RT_{ai}}\right) \mathrm{d}T = \frac{RT_{ai}^{2}}{E_{a}} \left[\frac{1 - \frac{2RT}{E_{a}}}{1 - 5\left(\frac{ER}{E_{a}}\right)^{2}}\right] \exp\left(\frac{-E_{a}}{RT_{ai}}\right)$$
(14)

$$\int_{0}^{T} \exp\left(\frac{-E_{a}}{RT_{ai}}\right) \mathrm{d}T = \frac{RT_{ai}^{2}}{E_{a}} \left[\frac{\frac{E_{a}}{RT_{ai}} + 0.66691}{\frac{E_{a}}{RT_{ai}} + 2.64943}\right] \exp\left(\frac{-E_{a}}{RT_{ai}}\right)$$
(15)

3.2.3. Compensation effect

The validity of the compensation effect is related to the linearity of the relationship between $\ln A$ and E_a for related chemical processes under different conditions utilizing various reaction models to the same set of nonisothermal kinetic data. The compensation effect is associated to artificial isokinetic relationship (IKR) when chemical reactions become identical at a certain isokinetic temperature T_{iso} which can be ascribed by Eq. (16):

$$\ln A_j = a + bE_{a,j} \tag{16}$$

Where *j* represents one of the possible models $f_i(\alpha)$ assumed to illustrate the reaction processes, a and b are constants corresponding to lnk_{iso} and 1/RT_{iso}, respectively. (Agrawal, 1986; Barrie, 2012; Bligaard et al., 2003; Cremer, 1955) Fig. 17 shows the artificial isokinetic relationship for the solid-state decomposition reactions of the un-irradiated and γ -irradiated tris(pentanedionato) iron (III) obtained by CK methods. The values of a, b, k_{iso} , T_{iso} of Eq. (16) attained by (CR and CK) modelfitting are given in Table 3. As shown the T_{iso} lie on experimental temperature region demonstrating that the reaction model $f_i(\alpha)$ was most likely selected. To estimate $\ln A_{\alpha}$ and illustrate it dependency on α for the un-irradiated and y-irradiated tris(pentanedionato) iron (III) decomposition process, the $E_{a,a}$ value were exchanged for $E_{a,i}$ in Eq. (16).(Al-Othman et al., 2009; Vyazovkin & Wight, 1999a) Fig. 18 shows $\ln A_{\alpha}$ relationship with α depicted form the applied isoconversional methods data for the decomposition processes of the un-irradiated and γ -irradiated tris(pentanedionato) iron (III) precursors with 100 and 300 kGy total dose ray, respectively. As exhibited, the $\ln A_{\alpha}$ dependency on the extent of the conversion (α) is quite similar with the apparent activation energy ($E_{a,\alpha}$) dependency on α in Fig. 16 supporting that the solid-state decomposition reaction of the un-irradiated and y-irradiated tris(pentanedionato) iron (III) precursors presumed to be a single step initially started with increasing $E_{a,a}$ and $\ln A_a$ with increasing the extant of conversion due to decomposition of organic moieties and the formation of active nucleation centres of iron oxide, and with 100 and 300 kGy radiation doses their values increased in comparison to un-irradiated sample attributed to the reduction of active nucleation sites during the decomposition reaction.

4. Conclusions

In conclusion, the investigation into the impact of γ -irradiation on tris(2,4-pentanedionato)iron(III) complexes has provided a comprehensive understanding of structural, morphological, and kinetic changes. The FTIR spectra revealed a decrease in intensity, particularly in the ν Fe-O bond region, indicating the influence of γ -irradiation on bond integrity. XRD patterns demonstrated that while the orthorhombic phase of tris(2,4-pentanedionato)iron(III) remained dominant, higher irradiation doses led to broadening and intensity loss, indicating decreased crystallinity and more significant damage. SEM images and EDS analysis confirmed the formation of spherical nanoparticles with minimal alteration under irradiation. TGA curves displayed subtle shifts in decomposition parameters, emphasizing the stability of the complex under γ -irradiation. Calcination revealed temperature-dependent phase transitions, with FTIR and XRD analyses indicating the successfully synthesized of iron oxide from direct pyrolysis of tris(pentanedionato) iron(III) singular molecular precursor in static air. The crystallite size reduction with increased irradiation suggests structural modifications induced by radiation. EDS analysis demonstrated changing molecular compositions, emphasizing radiation's impact on material structure. Kinetic studies revealed a single-step decomposition reaction proceed through two-dimensional diffusion (bi-dimensional particle shape) Valensi equation (D₂) as the stable nuclei would form slower than their subsequent growth rate, along with irradiation influencing activation energy and reaction rates. Isoconversional approaches highlighted enhanced porosity and surface reactivity. The compensation effect and $\ln A_{\alpha}$ relationship underscored the complex's dynamic response to irradiation. Overall, this study elucidates the intricate interplay of γ -irradiation on tris(2,4-pentanedionato)iron(III) complexes, providing valuable insights for tailoring these materials for various applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial



Fig. 18. The lnA dependence on the extent of the conversion for (a) un-irradiated, (b) γ -irradiated with 100 kGy, and (c) γ -irradiated with 300 kGy radiation doses.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The author acknowledges the Researchers Supporting Project number (RSP2023R243), King Saud University, Riyadh, Saudi Arabia.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.105531.

References

Agrawal, R.K., 1986. On the compensation effect. J. Therm. Anal. 31 (1), 73–86. https:// doi.org/10.1007/BF01913888.

- Al-Anazi, A., 2022. Iron-based magnetic nanomaterials in environmental and energy applications: a short review. Curr. Opin. Chem. Eng. 36, 100794 https://doi.org/ 10.1016/j.coche.2022.100794.
- Al-Othman, A.A., Al-Farhan, K.A., Mahfouz, R.M., 2009. Kinetic analysis of nonisothermal decomposition of (Mg5(CO3)4(OH)2·4H2O/5Cr2O3) crystalline mixture. Journal of King Saud University - Science 21 (2), 133–143. https://doi.org/ 10.1016/j.jksus.2009.04.001.
- Aly, S.A., Elembaby, D., 2020. Synthesis, spectroscopic characterization and study the effect of gamma irradiation on VO2+, Mn2+, Zn2+, Ru3+, Pd2+, Ag+ and Hg2+ complexes and antibacterial activities. Arab. J. Chem. 13 (2), 4425–4447. https:// doi.org/10.1016/j.arabjc.2019.08.007.
- Barrie, P.J., 2012. The mathematical origins of the kinetic compensation effect: 1. the effect of random experimental errors [10.1039/C1CP22666E]. PCCP 14 (1), 318–326. https://doi.org/10.1039/C1CP2266E.
- Bastami, T.R., Entezari, M.H., Hu, Q.H., Hartono, S.B., Qiao, S.Z., 2012. Role of polymeric surfactants on the growth of manganese ferrite nanoparticles. Chem. Eng. J. 210, 157–165. https://doi.org/10.1016/j.cej.2012.08.031.
- Bastami, T.R., Entezari, M.H., Kwong, C., Qiao, S., 2014. Influences of spinel type and polymeric surfactants on the size evolution of colloidal magnetic nanocrystals (MFe2O4, M= Fe. Mn). Frontiers of Chemical Science and Engineering 8 (3), 378–385. https://doi.org/10.1007/s11705-014-1441-y.
- Belaïd, S., Stanicki, D., Vander Elst, L., Muller, R.N., Laurent, S., 2018. Influence of experimental parameters on iron oxide nanoparticle properties synthesized by thermal decomposition: size and nuclear magnetic resonance studies. Nanotechnology 29 (16), 165603. https://doi.org/10.1088/1361-6528/aaae59.
- Bligaard, T., Honkala, K., Logadottir, A., Nørskov, J.K., Dahl, S., Jacobsen, C.J.H., 2003. On the Compensation Effect in Heterogeneous Catalysis. J. Phys. Chem. B 107 (35), 9325–9331. https://doi.org/10.1021/jp034447g.
- Brown, M.E., 1997. Steps in a minefield. J. Therm. Anal. 49 (1), 17–32. https://doi.org/ 10.1007/BF01987418.
- Carvalho, M.D., Henriques, F., Ferreira, L.P., Godinho, M., Cruz, M.M., 2013. Iron oxide nanoparticles: the Influence of synthesis method and size on composition and magnetic properties. J. Solid State Chem. 201, 144–152. https://doi.org/10.1016/j. jssc.2013.02.024.
- Choi, S.-H., Zhang, Y.-P., Gopalan, A., Lee, K.-P., Kang, H.-D., 2005. Preparation of catalytically efficient precious metallic colloids by γ-irradiation and characterization. Colloids Surf A Physicochem Eng Asp 256 (2), 165–170. https:// doi.org/10.1016/j.colsurfa.2004.07.022.
- Coats, A.W., Redfern, J.P., 1964. 1964/01/01). Kinetic Parameters from Thermogravimetric Data. *Nature* 201 (4914), 68–69. https://doi.org/10.1038/ 201068a0.
- Cornell, R. M., & Schwertmann, U. 2003. The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses. Wiley. https://books.google.com.sa/books? id=dlMuE3_klW4C.
- Cremer, E., 1955. The Compensation Effect in Heterogeneous Catalysis. In: Frankenburg, W.G., Komarewsky, V.I., Rideal, E.K. (Eds.), Advances in Catalysis, Vol. 7. Academic Press, pp. 75–91. https://doi.org/10.1016/S0360-0564(08)60525-8.
- Dudchenko, N., Pawar, S., Perelshtein, I., Fixler, D., 2022. Magnetite Nanoparticles: Synthesis and Applications in Optics and Nanophotonics. Materials 15 (7), 2601. https://www.mdpi.com/1996-1944/15/7/2601.
- Dudek, G., Turczyn, R., Djurado, D., 2020. Collation Efficiency of Poly(Vinyl Alcohol) and Alginate Membranes with Iron-Based Magnetic Organic/Inorganic Fillers in Pervaporative Dehydration of Ethanol. Materials 13 (18), 4152. https://www.mdpi. com/1996-1944/13/18/4152.
- El-Boraey, H.A., AboYehia, S.M., El-Gammal, O.A., 2022. Influence of high energy γ-irradiation on some binuclear transition metal complexes of pentadentate ligand: Spectral, thermal, modelling, X-ray diffraction, morphological and solid electrical conductivity. Appl. Radiat. Isot. 182, 110121 https://doi.org/10.1016/j. apradiso.2022.110121.
- Filippousi, M., Angelakeris, M., Katsikini, M., Paloura, E., Efthimiopoulos, I., Wang, Y., Zamboulis, D., Van Tendeloo, G., 2014. Surfactant Effects on the Structural and Magnetic Properties of Iron Oxide Nanoparticles. J. Phys. Chem. C 118 (29), 16209–16217. https://doi.org/10.1021/jp5037266.
- Flores-Rojas, G.G., López-Saucedo, F., Bucio, E., 2020. Gamma-irradiation applied in the synthesis of metallic and organic nanoparticles: A short review. Radiat. Phys. Chem. 169, 107962 https://doi.org/10.1016/j.radphyschem.2018.08.011.
- Flynn, J.H., Wall, L.A., 1966. Nov-Dec). General Treatment of the Thermogravimetry of Polymers. J Res Natl Bur Stand A Phys Chem 70a (6), 487–523. https://doi.org/ 10.6028/jrss.070A.043.
- Galwey, A.K., Brown, M.E., 1998. Chapter 3 Kinetic Background to Thermal Analysis and Calorimetry. In: Brown, M.E. (Ed.), Handbook of Thermal Analysis and Calorimetry, Vol. 1. Elsevier Science B.V, pp. 147–224. https://doi.org/10.1016/ S1573-4374(98)80006-X.
- Galwey, A.K., Brown, M.E., 2000. Solid-state Decompositions Stagnation or Progress? J. Therm. Anal. Calorim. 60 (3), 863–877. https://doi.org/10.1023/A: 1010107724523.
- Ibarra-Sánchez, J.J., Fuentes-Ramírez, R., Roca, A.G., del Puerto Morales, M., Cabrera-Lara, L.I., 2013. Key Parameters for Scaling up the Synthesis of Magnetite Nanoparticles in Organic Media: Stirring Rate and Growth Kinetic. Ind. Eng. Chem. Res. 52 (50), 17841–17847. https://doi.org/10.1021/ie403250p.
- Israel, L.L., Galstyan, A., Holler, E., Ljubimova, J.Y., 2020. Magnetic iron oxide nanoparticles for imaging, targeting and treatment of primary and metastatic tumors

of the brain. J. Control. Release 320, 45–62. https://doi.org/10.1016/j. jconrel.2020.01.009.

- Jurkin, T., Gotić, M., Štefanić, G., Pucić, I., 2016. Gamma-irradiation synthesis of iron oxide nanoparticles in the presence of PEO, PVP or CTAB. Radiat. Phys. Chem. 124, 75–83. https://doi.org/10.1016/j.radphyschem.2015.11.019.
- Kennedy, J.A., Clark, S.M., 1997. A new method for the analysis of non-isothermal DSC and diffraction data. Thermochim Acta 307 (1), 27–35. https://doi.org/10.1016/ S0040-6031(96)02962-0.
- Khawam, A., Flanagan, D.R., 2005. Role of isoconversional methods in varying activation energies of solid-state kinetics: II. Nonisothermal kinetic studies. Thermochim Acta 436 (1), 101–112. https://doi.org/10.1016/j.tca.2005.05.015.
- Kissinger, H.E., 1957. Reaction Kinetics in Differential Thermal Analysis. Anal. Chem. 29 (11), 1702–1706. https://doi.org/10.1021/ac60131a045.
- Kumar, P., Khanduri, H., Pathak, S., Singh, A., Basheed, G.A., Pant, R.P., 2020. Temperature selectivity for single phase hydrothermal synthesis of PEG-400 coated magnetite nanoparticles [10.1039/D0DT01318H]. Dalton Trans. 49 (25), 8672–8683. https://doi.org/10.1039/D0DT01318H.
- Laye, P. G., Warrington, S. B., Group, T. M., Heal, G. R., Price, D. M., Wilson, R., & Haines, P. 2007. Principles of Thermal Analysis and Calorimetry. Royal Society of Chemistry. https://books.google.com.sa/books?id=Rm0oDwAAQBAJ.
- Maity, D., Kale, S.N., Kaul-Ghanekar, R., Xue, J.-M., Ding, J., 2009. Studies of magnetite nanoparticles synthesized by thermal decomposition of iron (III) acetylacetonate in tri(ethylene glycol). J. Magn. Magn. Mater. 321 (19), 3093–3098. https://doi.org/ 10.1016/j.jmmm.2009.05.020.
- Marić, I., Gotić, M., Štefanić, G., Pustak, A., Jurkin, T., 2020. γ-irradiation generated ferrous ions affect the formation of magnetite and feroxyhyte. Radiat. Phys. Chem. 170, 108648 https://doi.org/10.1016/j.radphyschem.2019.108648.
- Miguel-Sancho, N., Bomati-Miguel, O., Roca, A.G., Martinez, G., Arruebo, M., Santamaria, J., 2012. Synthesis of Magnetic Nanocrystals by Thermal Decomposition in Glycol Media: Effect of Process Variables and Mechanistic Study. Ind. Eng. Chem. Res. 51 (25), 8348–8357. https://doi.org/10.1021/ie3002974.
- Muro-Cruces, J., Roca, A. G., López-Ortega, A., Fantechi, E., del-Pozo-Bueno, D., Estradé, S., Peiró, F., Sepúlveda, B., Pineider, F., Sangregorio, C., & Nogues, J. 2019. Precise Size Control of the Growth of Fe3O4 Nanocubes over a Wide Size Range Using a Rationally Designed One-Pot Synthesis. ACS Nano, 13(7), 7716-7728. https://doi. org/10.1021/acsnano.9b01281.
- Ngoi, K.H., Wong, J.C., Chiu, W.S., Chia, C.H., Jin, K.S., Kim, H.-J., Kim, H.-C., Ree, M., 2021. Morphological structure details, size distributions and magnetic properties of iron oxide nanoparticles. J. Ind. Eng. Chem. 95, 37–50. https://doi.org/10.1016/j. jiec.2020.11.027.
- Nguyen, T. K. L., Nguyen, N. D., Dang, V. P., Phan, D. T., Tran, T. H., & Nguyen, Q. H. 2019. Synthesis of Platinum Nanoparticles by Gamma Co-60 Ray Irradiation Method Using Chitosan as Stabilizer. Advances in Materials Science and Engineering, 2019, 9624374. https://doi.org/10.1155/2019/9624374.
- Pereira, C., Pereira, A.M., Fernandes, C., Rocha, M., Mendes, R., Fernández-García, M.P., Guedes, A., Tavares, P.B., Grenèche, J.-M., Araújo, J.P., Freire, C., 2012. Superparamagnetic MFe2O4 (M = Fe Co, Mn) Nanoparticles: Tuning the Particle Size and Magnetic Properties through a Novel One-Step Coprecipitation Route. Chem. Mater. 24 (8), 1496–1504. https://doi.org/10.1021/cm300301c.
- Petcharoen, K., Sirivat, A., 2012. Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. Mater. Sci. Eng. B 177 (5), 421–427. https://doi.org/10.1016/j.mseb.2012.01.003.
- Reading, M., 1998. Chapter 8 Controlled Rate Thermal Analysis and Related Techniques. In: Brown, M.E. (Ed.), Handbook of Thermal Analysis and Calorimetry, Vol. 1. Elsevier Science B.V, pp. 423–443. https://doi.org/10.1016/S1573-4374(98) 80011-3.
- Remita, S., Mostafavi, M., Delcourt, M.O., 1996. Bimetallic AgPt and AuPt aggregates synthesized by radiolysis. Radiat. Phys. Chem. 47 (2), 275–279. https://doi.org/ 10.1016/0969-806X(94)00172-G.
- Roca, A.G., Morales, M.P., Serna, C.J., 2006. Synthesis of Monodispersed Magnetite Particles From Different Organometallic Precursors. IEEE Trans. Magn. 42 (10), 3025–3029. https://doi.org/10.1109/TMAG.2006.880111.
- Roca, A.G., Gutiérrez, L., Gavilán, H., Fortes Brollo, M.E., Veintemillas-Verdaguer, S., Morales, M.D.P., 2019. Design strategies for shape-controlled magnetic iron oxide nanoparticles. Adv. Drug Deliv. Rev. 138, 68–104. https://doi.org/10.1016/j. addr.2018.12.008.
- Rodante, F., Vecchio, S., Tomassetti, M., 2002. Kinetic analysis of thermal decomposition for penicillin sodium salts: Model-fitting and model-free methods. Journal of Pharmaceutical and Biomedical Analysis 29 (6), 1031–1043. https://doi.org/ 10.1016/S0731-7085(02)00144-9.
- Saha, B., Ghoshal, A.K., 2006. Model-free kinetics analysis of waste PE sample. Thermochim Acta 451 (1), 27–33. https://doi.org/10.1016/j.tca.2006.09.001.
- Saha, B., Maiti, A.K., Ghoshal, A.K., 2006. Model-free method for isothermal and nonisothermal decomposition kinetics analysis of PET sample. Thermochim Acta 444 (1), 46–52. https://doi.org/10.1016/j.tca.2006.02.018.
- Sbirrazzuoli, N., Vyazovkin, S., 2002. Learning about epoxy cure mechanisms from isoconversional analysis of DSC data. Thermochim Acta 388 (1), 289–298. https:// doi.org/10.1016/S0040-6031(02)00053-9.
- Sharp, J.H., Brindley, G.W., Achar, B.N.N., 1966. Numerical Data for Some Commonly Used Solid State Reaction Equations [https://doi.org/10.1111/j.1151-2916.1966. tb13289.x]. J. Am. Ceram. Soc. 49 (7), 379-382. https://doi.org/10.1111/j.1151-2916.1966.tb13289.x.
- Siddiqi, M.A., Siddiqui, R.A., Atakan, B., 2007. Thermal stability, sublimation pressures and diffusion coefficients of some metal acetylacetonates. Surf. Coat. Technol. 201 (22), 9055–9059. https://doi.org/10.1016/j.surfcoat.2007.04.036.

Slabzhennikov, S.N., Ryabchenko, O.B., Kuarton, L.A., 2003. Normal Vibration Calculations for Iron Tris(acetylacetonate). Russ. J. Coord. Chem. 29 (7), 484–488. https://doi.org/10.1023/A:1024778929930.

Spinks, J.W.T., Woods, R.J., 1990. An Introduction to Radiation Chemistry. Wiley. https://books.google.com.sa/books?id=TQLwAAAAMAAJ.

- Stoia, M., Istratie, R., Păcurariu, C., 2016. Investigation of magnetite nanoparticles stability in air by thermal analysis and FTIR spectroscopy. J. Therm. Anal. Calorim. 125 (3), 1185–1198. https://doi.org/10.1007/s10973-016-5393-y.
- Sun, B.-W., Yu, H.-Y., Yang, Y.-J., Li, H.-J., Zhai, C.-Y., Qian, D.-J., Chen, M., 2017. New complete assignment of X-ray powder diffraction patterns in graphitic carbon nitride using discrete Fourier transform and direct experimental evidence [10.1039/ C7CP05242A]. PCCP 19 (38), 26072–26084. https://doi.org/10.1039/ C7CP05242A.
- Tang, T.B., Chaudhri, M.M., 1980. Analysis of dynamic kinetic data from solid-state reactions. J. Therm. Anal. 18 (2), 247–261. https://doi.org/10.1007/BF02055808
- Tayyari, S.F., Milani-nejad, F., 2000. Vibrational assignment of acetylacetone. Spectrochim. Acta A Mol. Biomol. Spectrosc. 56 (14), 2679–2691. https://doi.org/ 10.1016/S1386-1425(00)00304-8.
- Teja, A.S., Koh, P.-Y., 2009. Synthesis, properties, and applications of magnetic iron oxide nanoparticles. Prog. Cryst. Growth Charact. Mater. 55 (1), 22–45. https://doi. org/10.1016/j.pcrysgrow.2008.08.003.
- Torres-Gómez, N., Nava, O., Argueta-Figueroa, L., García-Contreras, R., Baeza-Barrera, A., & Vilchis-Nestor, A. R. 2019. Shape Tuning of Magnetite Nanoparticles Obtained by Hydrothermal Synthesis: Effect of Temperature. Journal of Nanomaterials, 2019, 7921273. https://doi.org/10.1155/2019/7921273.
- Toyos-Rodríguez, C., Calleja-García, J., Torres-Sánchez, L., López, A., Abu-Dief, A. M., Costa, A., Elbaile, L., Crespo, R. D., Garitaonandia, J. S., Lastra, E., García, J. A., & García-Alonso, F. J. 2019. A Simple and Reliable Synthesis of Superparamagnetic Magnetite Nanoparticles by Thermal Decomposition of Fe(acac)₃. Journal of Nanomaterials, 2019, 2464010. https://doi.org/10.1155/2019/2464010.
- Valenzuela, R., Fuentes, M.C., Parra, C., Baeza, J., Duran, N., Sharma, S.K., Knobel, M., Freer, J., 2009. Influence of stirring velocity on the synthesis of magnetite

nanoparticles (Fe3O4) by the co-precipitation method. J. Alloy. Compd. 488 (1), 227–231. https://doi.org/10.1016/j.jallcom.2009.08.087.

- van Ekeren, P.J., 1998. Chapter 2 Thermodynamic Background to Thermal Analysis and Calorimetry. In: Brown, M.E. (Ed.), Handbook of Thermal Analysis and Calorimetry, Vol. 1. Elsevier Science B.V, pp. 75–145. https://doi.org/10.1016/S1573-4374(98) 80005-8.
- Vyazovkin, S., 2000. Kinetic concepts of thermally stimulated reactions in solids: A view from a historical perspective. Int. Rev. Phys. Chem. 19 (1), 45–60. https://doi.org/ 10.1080/014423500229855.
- Vyazovkin, S., Wight, C.A., 1997. Isothermal and Nonisothermal Reaction Kinetics in Solids. In Search of Ways toward Consensus. Chem. A Eur. J. 101 (44), 8279–8284. https://doi.org/10.1021/jp971889h.
- Vyazovkin, S., Wight, C.A., 1999a. Kinetics of Thermal Decomposition of Cubic Ammonium Perchlorate. Chem. Mater. 11 (11), 3386–3393. https://doi.org/ 10.1021/cm9904382.
- Vyazovkin, S., Wight, C.A., 1999b. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochim Acta 340–341, 53–68. https://doi.org/10.1016/S0040-6031(99)00253-1.
- Waldron, R.D., 1955. 09/15/). Infrared Spectra of Ferrites. Physical Review 99 (6), 1727–1735. https://doi.org/10.1103/PhysRev.99.1727.
- Wu, K., Liu, J., Saha, R., Peng, C., Su, D., Wang, Y.A., Wang, J.-P., 2021. Investigation of Commercial Iron Oxide Nanoparticles: Structural and Magnetic Property Characterization. ACS. Omega 6 (9), 6274–6283. https://doi.org/10.1021/ acsomega.0c05845.
- Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X., Liu, Z.F., 2012. Use of iron oxide nanomaterials in wastewater treatment: A review. Sci. Total Environ. 424, 1–10. https://doi.org/10.1016/j. scitotenv.2012.02.023.
- Yadav, B., Singh, R., Vishwakarma, A., & Kumar, N. 2020. Facile Synthesis of Substantially Magnetic Hollow Nanospheres of Maghemite (γ-Fe2O3) Originated from Magnetite (Fe3O4) via Solvothermal Method. Journal of Superconductivity and Novel Magnetism, 33. https://doi.org/10.1007/s10948-020-05481-7.