



SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF MAGNETITE NANOPARTICLES (Fe_3O_4) AS POTENTIAL SOLID SUPPORT FOR HOMOGENEOUS CATALYSTS

(Sintesis dan Sifat Fizikokimia Nanopartikel Magnetit (Fe_3O_4) Sebagai Penyokong Pepejal Bagi Mangkin Homogen)

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Abstract

Black and dark magnetite nanoparticles (MNPs) were successfully synthesised through a co-precipitation method as a crucial material to support palladium(II) complexes as they have the potential to become a stable solid support for homogeneous systems. The two-hour synthesis was done by mixing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in an alkaline medium. To improve the properties of iron oxide nanoparticles, the process was done under inert conditions. The physicochemical properties of this support was then characterised using various spectroscopic techniques such as Fourier Transform Infrared (FTIR) spectroscopy that shows the X-ray diffraction analysis (XRD), Thermogravimetric analysis (TGA), Field Emission Scanning Electron Microscope (FESEM), and Vibrating Sample Magnetometer (VSM). The pore size distribution and the specific BET surface area were measured by N_2 adsorption-desorption isotherms. The FTIR absorption spectroscopy was used to confirm the formation of Fe-O bond. The most intense peak correspond to the (311) crystallographic orientation of the spinel cubic phase of MNPs shown by XRD pattern result. The particle size of magnetite was successfully controlled in the range of 20-40 nm. All of the MNPs showed the superparamagnetic behaviour with high saturation magnetization.

Keywords: magnetite nanoparticles, catalyst support, homogeneous catalysis, heterogeneous catalysis

Abstrak

Nanopartikel magnetit hitam legap telah berjaya disintesis dengan kaedah pemendakan kerana ianya penting untuk menyokong kompleks paladium(II) dan berpotensi menjadi penyokong padu yang stabil bagi sistem homogen. Sintesis selama dua jam dilakukan dengan mencampurkan $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dan $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dalam medium beralkali. Bagi meningkatkan sifat nanopartikel oksida besi, persekitaran proses perlu dilakukan dalam keadaan lengai. Sifat fizikokimia penyokong ini telah dicirikan oleh pelbagai teknik spektroskopi seperti Spektroskopi Inframerah (FTIR), Pembelauan Sinar-X (XRD), Analisis Gravimetri Terma (TGA), Mikroskopi Elektron Pengimbasan Pancaran Medan (FESEM), dan Magnetometer Getaran Sampel (VSM). Sebaran saiz liang dan luas permukaan BET yang tertentu diukur menggunakan teknik penjerapan dan penyahjerapan N_2 isoterma. Serapan FTIR spektroskopi digunakan untuk menentukan pembentukan ikatan Fe-O. Puncak yang paling tinggi merujuk kepada fasa kubik spinel dengan orientasi kristalografik (311) ditunjukkan oleh keputusan corak XRD. Saiz zarah magnetit berjaya dikawal dalam lingkungan 20-40 nm. Keseluruhan MNPs menunjukkan sifat ketepatan pemagnetan yang tinggi.

Kata kunci: nanopartikel magnetit, sokongan mangkin, pemangkinan homogen, pemangkinan heterogen

Introduction

Limitations on the catalyst separation becoming one of the drawbacks of homogeneous reaction systems, various approaches using solid materials as catalyst support have been extensively studied [1]. To date, considerable research attention has been paid to the usage of supported catalysts for organic synthesis. According to Lim and Lee, the heterogeneous catalytic system provides benefits as it can simply separate and purify organic reactions [2]. Nowadays, Fe₃O₄ magnetite nanoparticles (MNPs) have become a prominent support to catalyst due to its special properties including high surface area, super-paramagnetism, low toxicity and potential applications in various fields [3]. In huge industries, the usage of green catalysts are very crucial as economical catalysts can be re-used several times and produce low levels of contamination in the final products. In addition, the unique properties of Fe₃O₄ MNPs such as easy to separate using external magnets [4] and favorable in surface functionalisation promises excellent support as green catalysts. There are several methods to synthesise magnetic Fe₃O₄ nanoparticles such as hydrothermal synthesis, thermal decomposition, micro-emulsion and co-precipitation. However, the co-precipitation method is considered the ideal method as it is characterised by a low temperature, short reaction time and high reaction yield [5]. This paper is devoted to explaining the process of synthesising MNPs using the co-precipitation method and characterising the magnetite's behaviour using FTIR, XRD, FESEM, TGA, VSM and N₂ adsorption-desorption isotherms.

Materials and Methods

Reagents

The chemicals used in the experimental work-up are Iron(III) chloride hexahydrate, Iron(II) chloride tetrahydrate, tetraethyl orthosilicate (TEOS) and ammonia which were purchased from the standard chemical suppliers such as Sigma Aldrich and MERCK Chemical Co. Materials were used as received without any further purification or any special precautions during the experimental work-up.

Characterisation

The infrared (IR) spectrum was recorded on a Perkin Elmer 100 Fourier Transform Infrared Spectroscopy in the range of 4000-400 cm⁻¹ using potassium bromide (KBr) pellets. The X-ray diffraction (XRD) pattern was recorded on a Rigaku MiniFlex II Advanced X-ray diffractometer with a Cu K α radiation ($\gamma = 1.5418$) in the range of 15-80 ° of a 2 θ scale with a scanning speed of 0.03 °/s. The stability of compound was performed using a Perkin Elmer TGA Analyzer (Perkin Elmer Pyris 6 TGA) from 25 °C to 950 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The magnetisation of Fe₃O₄ was measured using a vibrating sample magnetometer (VSM) model LakeShore / 7404. The magnetisation curve consisted of 133 points taken at a scan speed of 8 s/point and was measured under a magnetic field strength of 14,000 Gauss (G) at room temperature. The morphological image was taken using a JEOL JSM-6701F Field Emission Scanning Electron Microscope (FESEM) at a 10kV acceleration voltage with magnifications n of 50000x and 100000x. The specific Brunauer-Emmett-Teller (BET) surface area and pore size measurements were performed using a Micromeritics ASAP 2020 instrument.

Synthesis of magnetite Fe₃O₄ nanoparticles (MNPs)

The co-precipitation method was used to synthesis the magnetite iron oxide nanoparticles [6,7,8] and its aqueous stabilisation [9]. The formation of nanoparticles was confirmed by the black color precipitate acquired by the mixture [10]. A mixture of FeCl₂.4H₂O (1.0 g, 5.0 mmol) and FeCl₃.6H₂O (2.6 g, 9.6 mmol) was prepared in 100 mL distilled water under vigorous stirring and in the presence of N₂ gas [11]. Then, the solution was added dropwise to 10 mL ammonia solution (NH₄OH 25 wt.%, excess). The reaction was heated at 70 °C for 2 hours. After cooling to room temperature, the black solid products were separated using a centrifuge. The precipitates were washed with deionised water and ethanol until it achieved a neutral pH reading. Finally, the magnetite Fe₃O₄ nanoparticles were dried in an oven for 24 hours at 80 °C.

Results and Discussion

The magnetite Fe₃O₄ nanoparticles were produced using the chemical co-precipitation of FeCl₂.4H₂O and FeCl₃.6H₂O, using ammonium hydroxide as the precipitating agent [8]. This synthesis was carried out using

aqueous mixture Fe^{2+} and Fe^{3+} chloride at 1:2 molar ratio to produce Fe_3O_4 [12]. The overall chemical reaction is written as equation 1 below:



The FTIR spectrum and absorption bands of the synthesised magnetite iron oxide nanoparticles are shown in Figure 1. The infrared spectrum of these iron oxide nanoparticles revealed all the expected bands of interest which are $\nu(\text{Fe-O})$ and $\nu(\text{Fe-OH})$. For the magnetites, the band at the range of $579\text{-}635\text{ cm}^{-1}$ corresponds to the vibration of the Fe-O bonds. Additionally, two bands of $\nu(\text{Fe-OH})$ were identified at 1609 and 3369 cm^{-1} , respectively, representing the stretching vibration of the hydroxyl groups on the surface of the MNPs which is in close agreement with previous reported [8, 13].

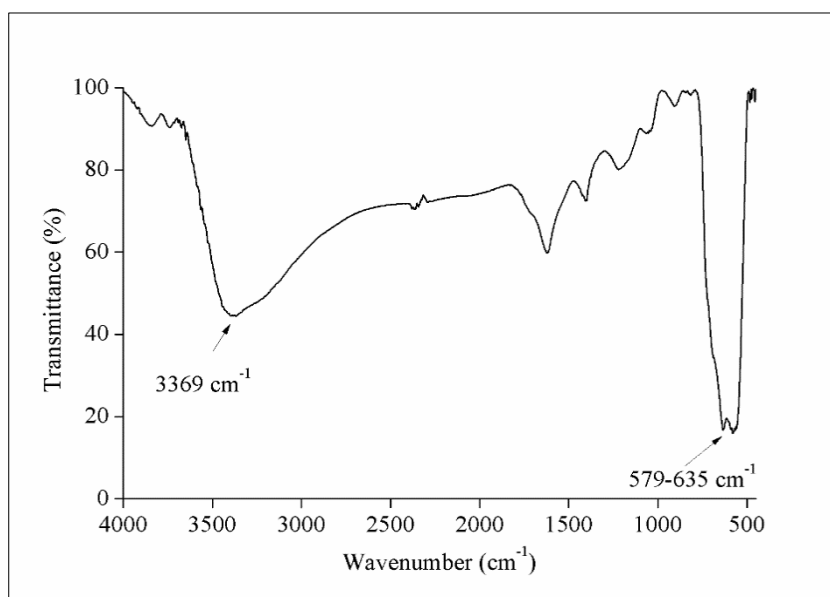


Figure 1. FT-IR spectrum of iron oxide (Fe_3O_4) nanoparticles

The phase identification and crystalline structure of the as-prepared black MNPs were determined using X-ray powder diffraction. As shown in Figure 2, the diffraction peaks of the sample could be readily assigned to Fe_3O_4 in accordance with the main characteristic peaks for magnetite reported in literature [11, 14, 15] and the standard values of Fe_3O_4 (PDF card 75-449). The diffraction peaks at (220), (311), (400), (422), (511) and (440) of the crystalline Fe_3O_4 nanoparticles reflect magnetite crystals with a cubic spinel structure [16]. The diffraction peaks obtained imply no other phase as impurities were detected in the sample. Generally, diffraction peaks were obtained for maghemite and hematite at (113), (210), (213) and (210), respectively [17]. However, these peaks do not appear in the XRD pattern.

An estimation of the magnetite Fe_3O_4 nanoparticles' size was performed using the Scherrer's formula. Particle size is calculated using the following equation 2 [18]:

$$d = \frac{k\lambda}{(\beta \cos \theta)} \quad (2)$$

where d is the particle size of magnetite; k is the shape parameter, also known as the Scherrer constant which is 0.9 for magnetite; λ is the X-ray wavelength ($\text{Cu K}\alpha = 1.5418\text{\AA}$); β is the full width at half maximum (FWHM); and θ is

the corresponding Bragg diffraction [13]. Taking the highest intensity peak namely the (311) plane at $2\theta = 35.5^\circ$ and the half maximum intensity of the peak after accounting for instrument broadening, the calculated particle size is 12 nm.

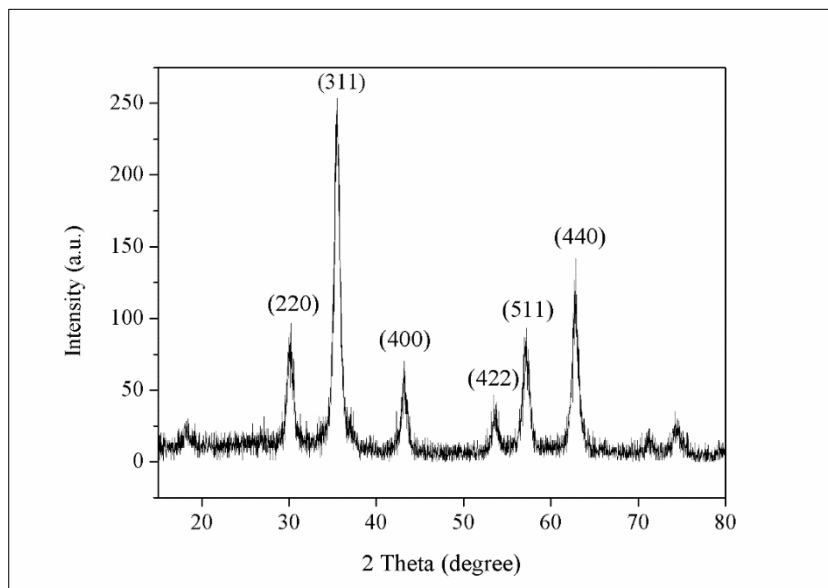


Figure 2. XRD pattern of Fe_3O_4 nanoparticles

The morphology of the magnetite Fe_3O_4 was identified using FESEM. As shown in Figure 3a, the morphology of the non-uniform distributed nanoparticles were observed. The FESEM image at higher magnification (Figure 3b) revealed that the resultant nanoparticles were measured to be 20-40 nm in average. Through observation, the particles have a larger size compared to the result obtained from the Scherrer equation due to aggregation between the particles [18].

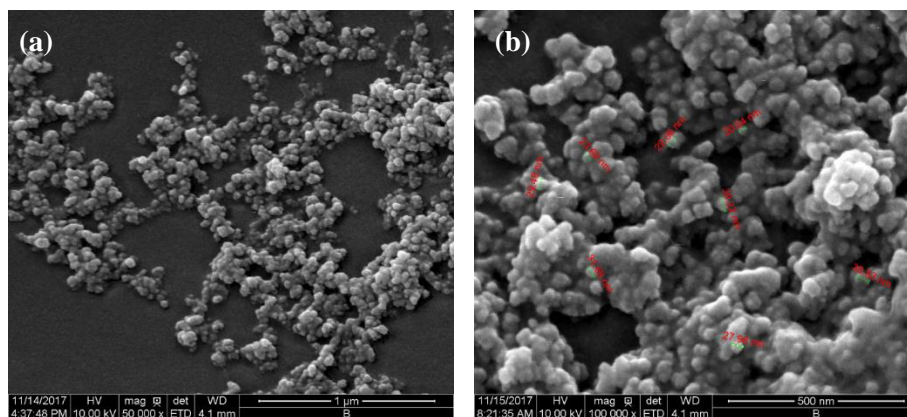


Figure 3. FESEM images of Fe_3O_4 nanoparticles. Scale bar (a) 1 μm and (b) 500 nm

The TGA curve of the magnetite Fe_3O_4 is shown in Figure 4. There are three mass losses in the TGA curve. The first degradation peak is at about 30-200 $^\circ\text{C}$, which is around the boiling or evaporation point of absorbed water molecules [11]. The second peak is at the range of 250-400 $^\circ\text{C}$ and the percentage of mass loss is about 9%, which

confirms the physisorption and chemisorption processes occurring at the surface of the MNPs [19]. The third peak is at the range 500-750 °C where the percentage of mass loss is about 4% attributed to the phase transition from magnetite to hematite [20]. As seen in Figure 4, the thermal stability of the Fe₃O₄ nanoparticles was estimated at temperatures up to 250 °C.

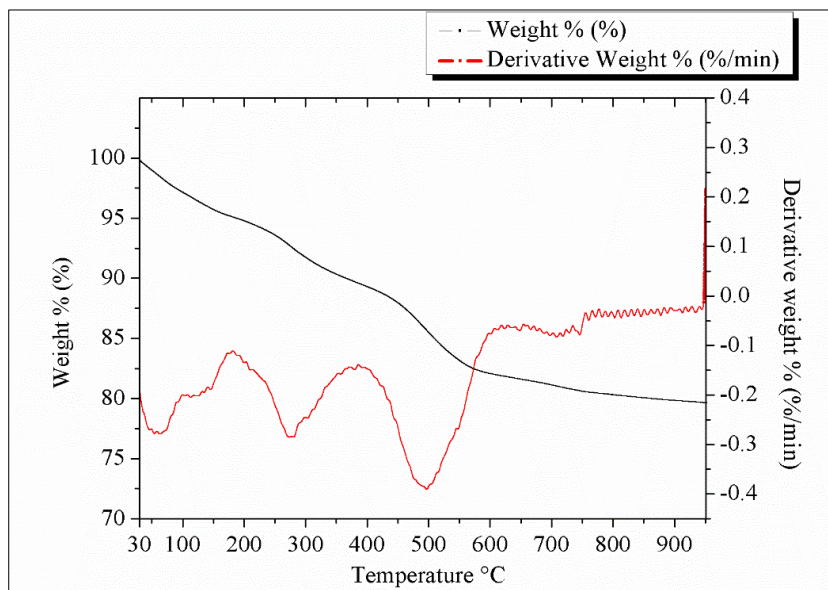


Figure 4. TGA curve of Fe₃O₄ nanoparticles

The magnetisation curve measured at room temperature for the synthesised magnetite Fe₃O₄ is given in Figure 5a. The curve indicates a superparamagnetic behaviour of the studied sample [8]. It is clear that the values of remanence (Mr) and coercivity (Hc) on the magnetisation loop which are close to zero verify the strong magnetic properties of synthesised Fe₃O₄ [21]. The saturation magnetisation (M_s) value was measured to be 54.85 emu g⁻¹ for Fe₃O₄ which is consistent with the value reported in the literature [16]. Superparamagnetism is an important and crucial property for reusable catalysts which are responsive to an applied magnetic field without permanent magnetisation. The magnetic response of Fe₃O₄ was tested by placing a magnetic bar near the glass bottle (Figure 5b). The black particles were attracted towards the magnet; therefore the magnetite Fe₃O₄ can be easily separated from the catalytic reaction under an external magnetic field.

The specific Brunauer-Emmett-Teller (BET) surface area and the pore size distribution measurements of the sample were obtained from adsorption-desorption isotherms. The values dependent on the size and shape of the particles. The surface area and pore volume are crucial aspects as they can influence the distribution of active component for catalytic activity [22]. The effective surface area and high pore volume potentially increase the catalytic performance as the rising of the metal loading on the surface of catalyst [23]. The sample was found to possess a surface area of 93.67 m²g⁻¹ and a pore volume of 0.29 cm³ g⁻¹ with an average pore diameter of 12.34 nm (Table 2). The specific surface area and average pore diameter of synthesized magnetite Fe₃O₄ nanoparticles are lower than values corresponding to the reported iron oxide due to the agglomeration of particles [24]. In this study, the magnetite Fe₃O₄ nanoparticles obtained were surfactant free which affected the surface area as well as pore size of sample.

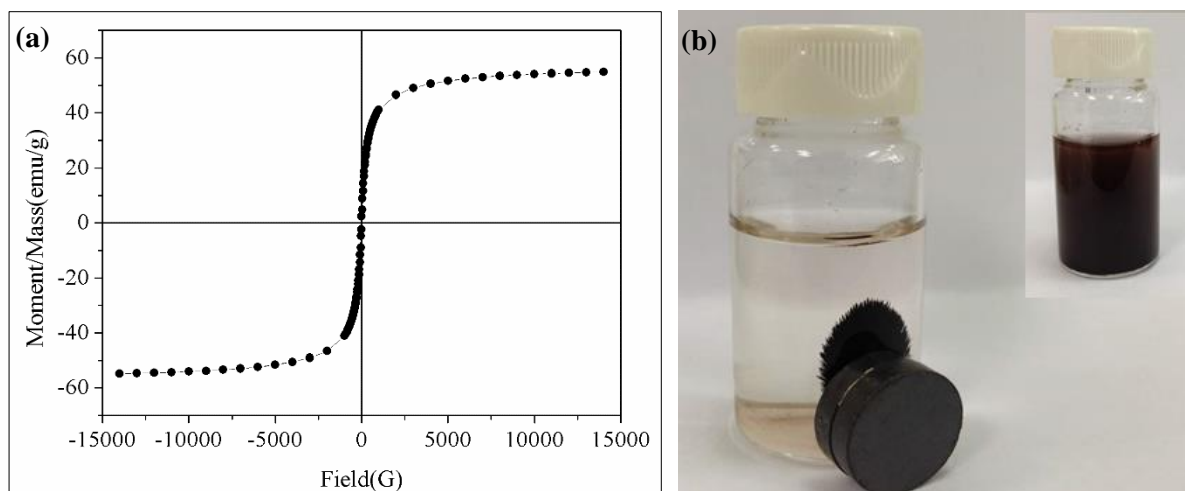


Figure 5. (a) VSM curve of Fe₃O₄, (b) Separation of Fe₃O₄ using an external magnet

Table 2. BET results of Fe₃O₄

Sample	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
Fe ₃ O ₄	93.67	0.29	12.34

Conclusion

This study investigated the synthesis of superparamagnetic Fe₃O₄ nanoparticles prepared using the co-precipitation method. The results show that the properties of the synthesised particles appear to be very promising as a solid support for heterogeneous catalysts. This is due to the thermal stability of the MNPs up to 250 °C, along with its high surface area and effective reclamation through the application of an external magnetic field. The synthesized supported material ease to recover from catalytic system as it can be reduced the formation of waste as well as economically.

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