

SYNTHESIS, CHARACTERIZATION AND ELECTRO CHEMICAL ACTIVITY OF Fe₂O₃

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Abstract:

Metal oxides constitute the most common, most diverse and fascinating class of materials in terms of electronic structure and physical, chemical and structural properties. Iron oxides are one of the most important transition metal oxides of technological importance. In recent years, magnetic nano-particles have attracted considerable attention not only for fundamental research, but for broad range of applications due to unique magnetic properties. Among these magnetic nano-materials, iron oxides (Fe₂O₃ and Fe₃O₄) have been extensively investigated because of its excellent magnetic properties and biocompatibility. The most conventional method for obtaining Fe₃O₄ & γ -Fe₂O₃ is by co-precipitation. Co-precipitation method is the most simple and effective way to prepare magnetic nanoparticles. In the room temperature or rising temperature, add alkaline matter into Fe²⁺/Fe³⁺ salt solution to prepare iron oxide nano-particles (Fe₃O₄, γ -Fe₂O₃). The prepared Fe₃O₄ and γ -Fe₂O₃ nanoparticles were dried with the help of a muffle furnace at 500 C to get a constant weight. The prepared materials were treated with a temperature of 400oc at 2hrs, 4hrs and 6hrs. Four different samples were characterized with SEM and their electrochemical properties were studied through Autolab-Electro chemical workstation. From SEM images, it was found that the size of the nanoparticles decreases as the amount of ageing time increases. The average size of the nanoparticles is estimated to be 50-200 nm, and 40-100 nm respectively. According to Liang et al, the influence of temperature on the synthesis of Fe₂O₃ nanoparticles is also significant. It is reported that an increase in the temperature or increased time duration of the synthetic system influences the phase of product. From the voltammograms, it can be clearly observed that the current response of the Fe₂O₃ electrodes in 1M H₂SO₄ electrolyte is greater than the other composite electrodes, implies the most superior capacitive performance is achieved for such composition.

Keywords: Co-precipitation, Fe₂O₃, nanoparticle.

I. Introduction:

Metal oxides have a wide range of applications, including transparent electronics, (chemical- , gas- , bio) sensors, piezoelectric transducers, light emitting devices, fuel cells, solar cells, support for catalysts etc.

The diversity of such application originates from the more complex crystal and electronic structures compared to other class structures. The main reasons are related to their variety of oxidation states, co- ordination number, symmetry, ligand field stabilization, density, stoichiometry and acid- base properties. As research progressed, it was found that mixtures of these metal oxides showed even more unique properties. The catalytic properties of existing known metal oxide catalysts can be enhanced by tailoring their micro and nanostructures. They may come in the form of either new oxides or new composite materials containing polymers and oxide blends or the new properties associated with nano structured materials.

Recent studies have shown that the electrocatalytic activity and chemical or mechanical stability of oxide electrodes are enhanced by incorporating/ doping other metal ions into the oxides.

1.1 Iron oxide nano particles

Iron oxides are one of the most important transition metal oxides of technological importance. Magnetic materials, especially iron oxide nano particles, are known since ancient times to have many spectacular properties, but in the last decade the properties that they possess at nanometric scale have been the starting point of great potential applications such as drug delivery[1-3]., magnetic cell separation, tumor labelling and cell labelling, which are widespread in nature and can be readily synthesized in the laboratory. Magnetic IONPs are inexpensive to produce, physically and chemically stable, biocompatible, and environmentally safe [4]. Eight iron oxides are known [5], among these iron oxides, hematite (α - Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ - Fe_2O_3) are very promising and popular candidates due to their polymorphism involving temperature-induced phase transition. Each of these three iron oxides has unique biochemical, magnetic, catalytic, and other properties which provide suitability for specific technical and biomedical applications.

1.2 Need for the synthesis of Fe_2O_3 nano particles

Nanosized iron oxides have considerable attention due to their unique magnetic properties (superparamagnetism, low curie temperature, high magnetic susceptibility, nontoxicity, biocompatibility, and low cost of production), which allow their usage in various nanotechnology applications in a broad range of disciplines [6-8].

These oxides find applications as catalysts, sorbents, pigments, flocculants, coatings, gas sensors, ion exchangers and for lubrication [9]. Iron oxide nano-composites have potential applications in areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging, wastewater treatment, bioseparation, and medicine[10]. Below a critical size, Fe_2O_3 nanoparticles can be used for niche applications like transparent iron oxide

pigments, due to their durability, shade, UV absorption and added value[11]. Careful control of the preparation process of transparent iron oxide pigments results in the formation of pigments with very small primary particle sizes. When fully dispersed, they do not scatter light and are hence completely transparent.

Recent progress in the use of magnetic nano- and micro-particles for biomedical applications has significantly exceeded expectations. The versatile intrinsic properties of magnetic particles enable their use in numerous medical applications.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Synthesis of iron oxide nano particles

In recent years, magnetic nano-particles have attracted considerable attention not only for fundamental research, but for broad range of applications due to unique magnetic properties. Among these magnetic nano-materials, iron oxides (Fe_2O_3 and Fe_3O_4) have been extensively investigated because of its excellent magnetic properties and biocompatibility. For more than 10 years in the past, people have been doing a lot of research on the preparation of iron oxide nano-particles. Many methods have been reported to prepare monodisperse, shape controllable and biocompatible ferric oxide nano-particle. The most commonly-used methods include co-precipitation method, pyrolytic process, hydro-thermal method, microemulsion and sonochemical method. There are some other methods such as electrochemical synthesis, laser pyrolysis technology and microbiological or bacterial synthesis. The commonly-used precursors to prepare mono-disperse iron oxide nano-particles include FeCl_2 , FeCl_3 , $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_2$, $\text{Fe}(\text{SO}_4)_3$, $\text{Fe}(\text{acac})_3$, iron acetate, iron oleate, etc. The most conventional method for obtaining Fe_3O_4 and γ - Fe_2O_3 is by co-precipitation.

2.2 Co-precipitation method

Co-precipitation method is the most simple and effective way to prepare magnetic nanoparticles. In the room temperature or rising temperature, add alkaline matter into $\text{Fe}^{2+}/\text{Fe}^{3+}$ salt solution to prepare iron oxide nano-particles (Fe_3O_4 , γ - Fe_2O_3). In the process of co-precipitation, salt varieties [FeCl_3 , FeSO_4 , $\text{Fe}(\text{NO}_3)_3$, FeClO_4], pH value, ionic strength, temperature and $\text{Fe}^{2+}/\text{Fe}^{3+}$ concentration ratio were used to adjust the dimension and shape of iron oxide nano-particles. In recent years, some people used co-precipitation method to produce iron oxide nano-particles with a dimension of 2-17 nm. They also studied the influence of different parameters $\text{Fe}^{2+}/\text{Fe}^{3+}$ concentration ratio, temperature, injection flow, the concentration of Fe^{2+} , Fe^{3+} and TMAOH) on the dimension and magnetism of the particle. The product prepared by this method has good super paramagnetic behaviour but α - Fe_2O_3 and γ - Fe_2O_3 appeared in the process of annealing. This method is simple, effective and easy to adjust to massive production. Iron oxide nano-particles that are prepared have a wider range of dimensions, sometimes you need to have a second choice of dimensions. A wider range of dimensions of the particles will lead to a wider range of

block temperature and as the block temperature depends on the dimension of the particle, ideal magnetism cannot be reached in many application fields.

The wet chemical synthesis of Fe_3O_4 nanoparticles was based on hydrolysis of Fe^{3+} and Fe^{2+} salts in the presence of urea and NaOH [12] with the following ultrasonic treatment of $FeO(OH)/Fe(OH)_2$. The synthesis of Fe_3O_4 is shown in flowchart.

5.41g of $FeCl_3 \cdot 6H_2O$ and 3.6g of $(NH_2)_2CO$ were dissolved in 200ml of distilled water in a container. It was placed in a water bath at constant temperature $85\text{ }^\circ\text{C}$ – $95\text{ }^\circ\text{C}$ for 2 hours. A khaki slurry coloured solution of $FeO(OH)$ precipitations was cooled down to $20\text{ }^\circ\text{C}$ and 1.99g of $FeSO_4 \cdot 7H_2O$ was dissolved in the above mixture. It was stirred to 546 rpm/10 minutes and NaOH(2mol/L) was added until the pH > 10. A Greenish precipitate was formed.

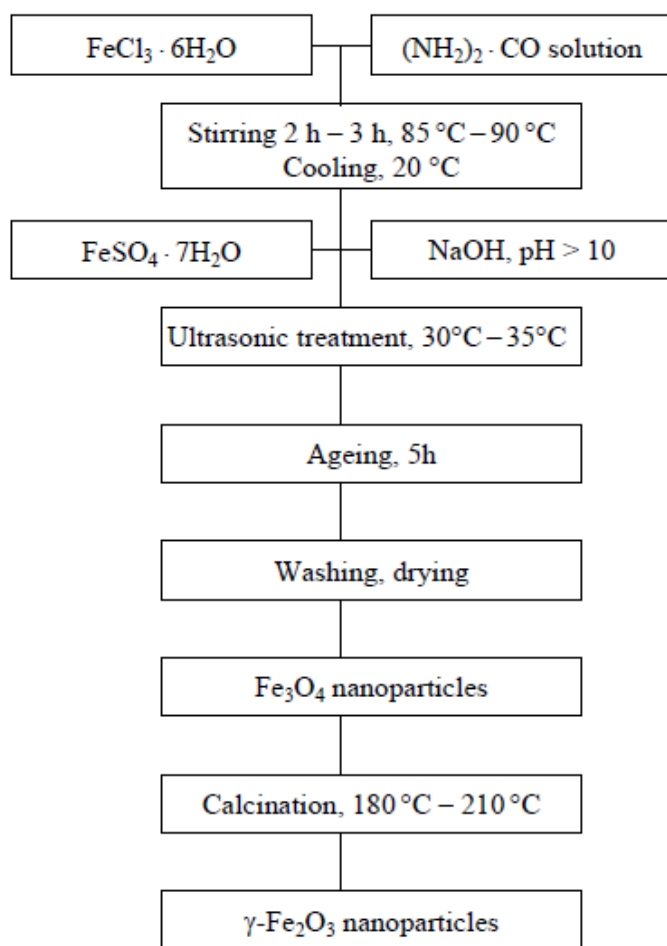


Fig.1 Synthesis of Fe_2O_3 nano particles
The $FeO(OH)/Fe(OH)_2$ precipitation was treated by ultrasound in the sealed flask at $30\text{ }^\circ\text{C}$ – $35\text{ }^\circ\text{C}$ for 10 min – 30 min in order to enhance interaction between the hydrolysis products. After ageing for 5 hr the obtained black powder was washed and

dried and separated by filtration. The calcinations of the prepared Fe_3O_4 powder in air at temperature $180\text{ }^\circ\text{C}$ – $210\text{ }^\circ\text{C}$ led to formation of $\gamma\text{-Fe}_2\text{O}_3$. The prepared Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were dried with the help of a muffle furnace at $500\text{ }^\circ\text{C}$ to get a constant weight. The prepared materials were treated with a temperature of $400\text{ }^\circ\text{C}$ at 2hrs, 4hrs and 6hrs . Four different samples were characterized with SEM and their electrochemical properties were studied through Autolab-Electro chemical workstation.

2.3 Scanning Electron Microscopy:

Scanning electron microscopy (SEM) is a well-known physical characterization technique that is utilized for observing the morphology of a sample at high magnification. SEM can be coupled with energy dispersive X-ray (EDX) analysis to determine elemental composition as well as other properties such as electro conductivity of a sample. The device takes advantage of electrons having a particular wavelength to act like photons. These wavelengths were hypothesized by de Broglie stating that the wavelength of matter is inversely proportional to the momentum of a particle and that the frequency is directly proportional to the particle's kinetic energy.

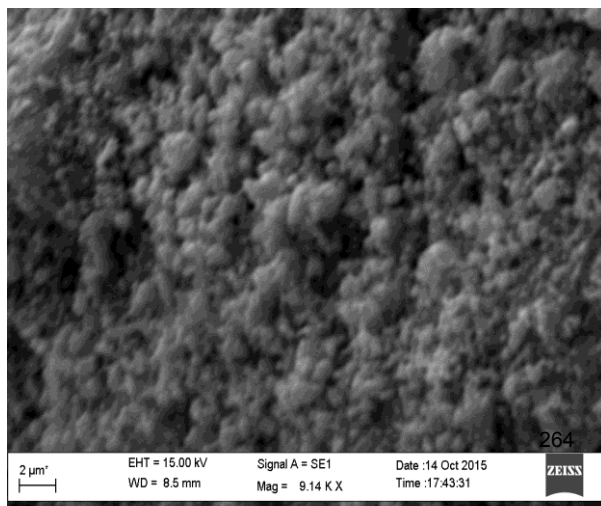
2.4 Cyclic Voltammetry

Cyclic Voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode, and measuring the resulting current.

2.5 Electrochemical Measurements

The electrocatalytic activities of the prepared catalysts were evaluated towards methanol electrooxidation reaction (MOR) in a standard three electrodes electrochemical cell.

Electrochemical measurements were carried out using a potentiostat AUTOLAB 128N (Ecochemie, The Netherlands) interfaced with software NOVA interface (version 1.9) with conventional three electrode cell comprising a GC working electrode, Pt foil as the counter electrode and Ag/AgCl electrode as the reference electrode. Cyclic Voltammetric (CV) studies were performed in a solution containing $1.0\text{ M CH}_3\text{OH}$ solution in $0.5\text{ H}_2\text{SO}_4$ at a scan rate of 0.1 V/s . Prior to the measurements nitrogen gas was purged for nearly 30 min, and stable and reproducible voltammograms were recorded after cycling in the potential region between 0 V and 1.2 V (vs Ag/AgCl) in $0.5\text{ M H}_2\text{SO}_4$ solution at $25\text{ }^\circ\text{C}$. These voltammograms indicated that the catalysts were stable under the experimental conditions.



3. Results:

Fig.2a SEM Image of γ -Fe₂O₃ (untreated) with magnification of 2 μ m.

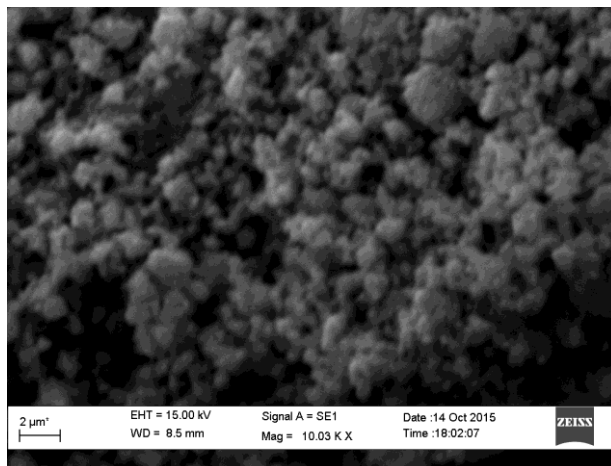


Fig.2b. SEM Image of γ -Fe₂O₃(400^oC-2hrs) with magnification of 2 μ m

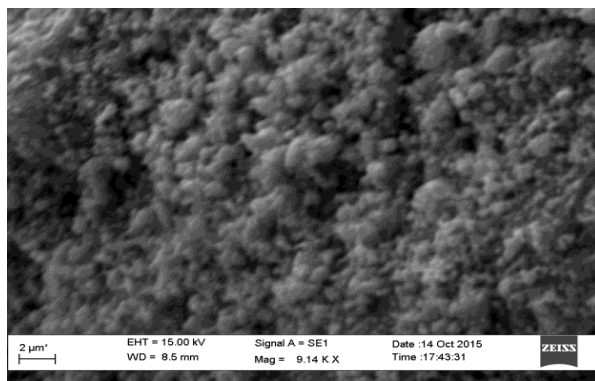


Fig.2c. SEM Image of γ -Fe₂O₃(400^oC-4hrs) with magnification of 2 μ m

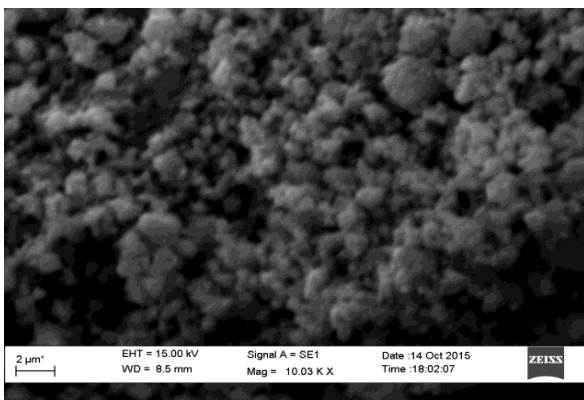


Fig.2d. SEM Image of $\gamma\text{-Fe}_2\text{O}_3(400^\circ\text{C-6hrs})$ with magnification of $2\mu\text{m}$

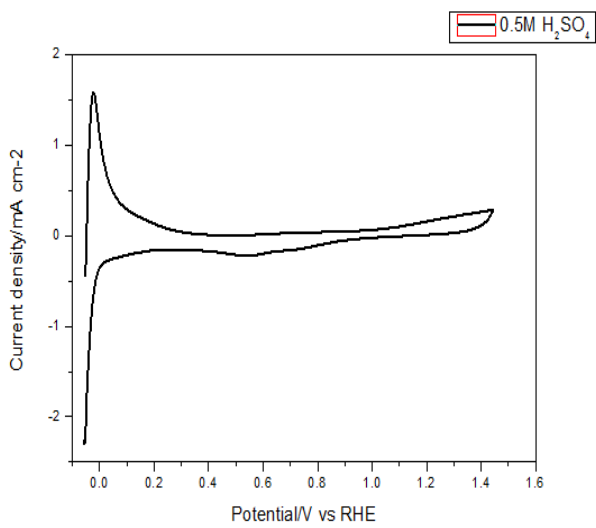


Figure 3a Cyclicvoltammogram of methanol oxidation catalysed byPt- Fe₂O₃ in N₂ saturated 0.5M H₂SO₄ at 25°C, scan rate 0.1V/s

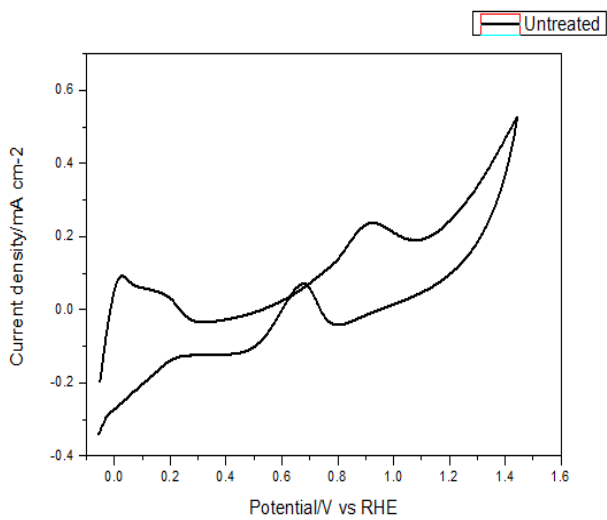


Fig. 3b Cyclicvoltammogram of

methanol oxidation catalysed by Pt-Fe₂O₃ (Untreated) in N₂ saturated 0.5M H₂SO₄ +1.0M methanol at 25°C, scan rate 0.1V/s

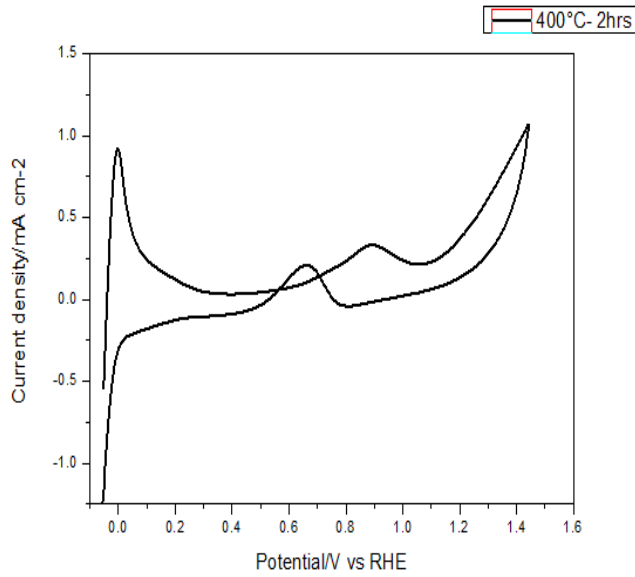


Fig. 3c Cyclicvoltammogram of methanol oxidation catalysed by Pt-Fe₂O₃ (400°C-2hrs) in N₂ saturated 0.5M H₂SO₄ +1.0M methanol at 25°C, scan rate 0.1V/s

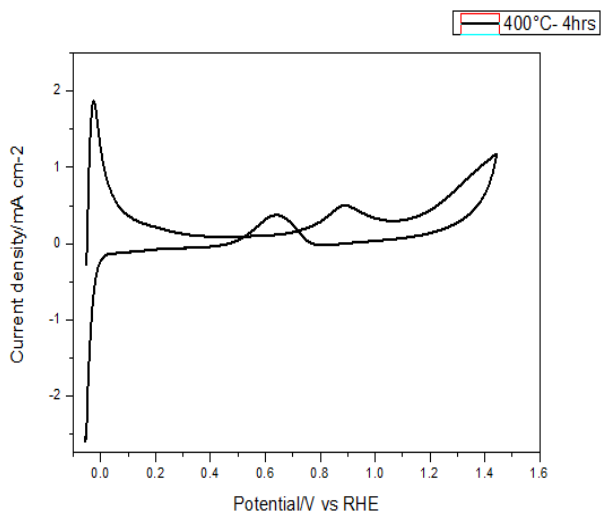


Fig. 3d Cyclic voltammogram of methanol oxidation catalysed by Pt-Fe₂O₃ (400°C-4hrs) in N₂ saturated 0.5M H₂SO₄ +1.0M methanol at 25°C, scan rate 0.1V/s

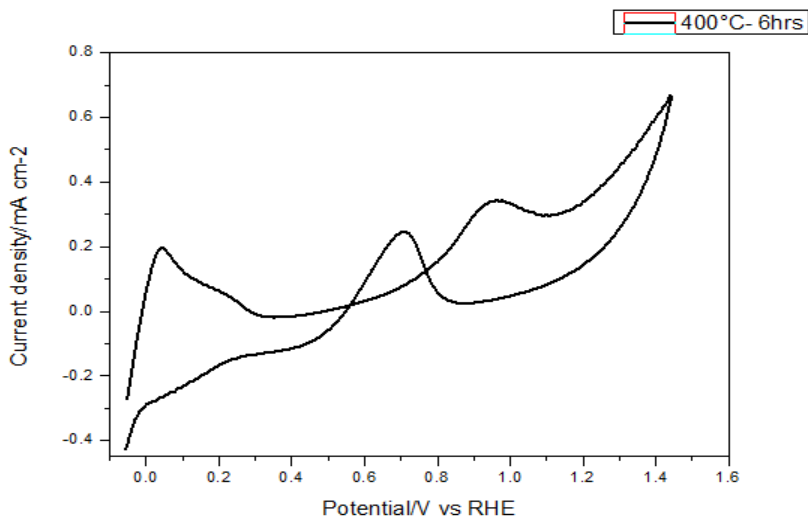


Fig. 3e Cyclicvoltammogram of methanol oxidation catalysed byPt-Fe₂O₃ (400°C-6hrs) in N₂ saturated 0.5M H₂SO₄ +1.0M methanol at 25°C, scan rate 0.1V/s

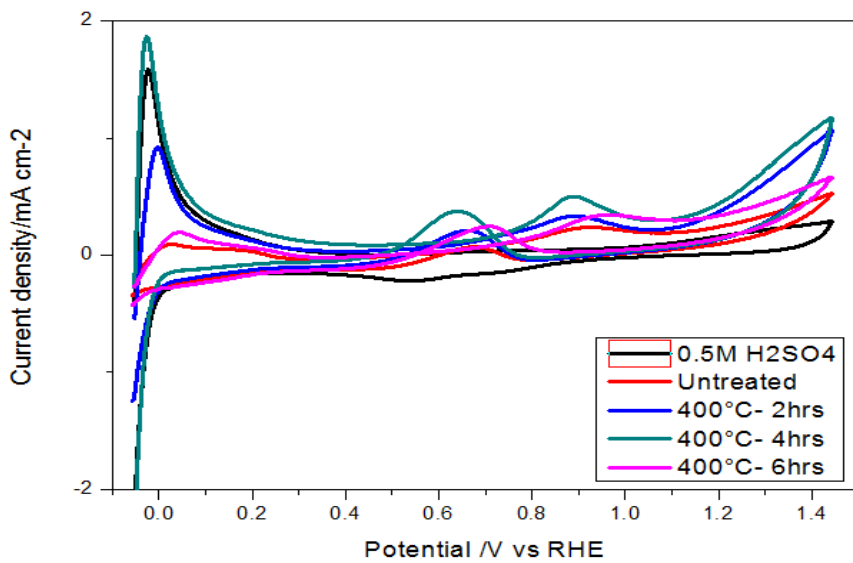


Fig. 3f Cyclic voltammogram of methanol oxidation catalysed by Pt-Fe₂O₃ (0.5M H₂SO₄, Untreated, 400°C-2hrs,4hrs,6hrs) in N₂ saturated 0.5M H₂SO₄ +1.0M methanol at 25°C, scan rate 0.1V/s

Table 1

Comparative performance of Pt-Fe₂O₃ heated to 400°C at different time intervals (Untreated, 400°C-2hrs,4hrs,6hrs) in methanol oxidation with 0.5M H₂SO₄ +1.0M methanol at 25°C

S.No	Fe ₂ O ₃ Nanoparticles	Forward peak current density	Backward peak current density	Forward peak potential	Backward peak potential	I _f /I _b
		(mA cm ⁻²)	(mA cm ⁻²)	(V)	(V)	
1	untreated	0.25714	0.0714	0.9	0.666	3.601
2	400°C-2hrs	0.35714	0.19642	0.8833	0.650	1.818
3	400°C-4hrs	0.5	0.333	0.8666	0.633	1.501
4	400°C-6hrs	0.332	0.248	0.932	0.680	1.338

4. Discussion:

A scanning electron microscopy was employed to analyse the structure of nanoparticles. Figs.2a and 2c show the low magnification (9.14 kx) SEM image of Fe₂O₃ powder, it can be seen that the particles are agglomerated.

The size distribution and morphology is irregular. The particles are plate like structure with coarsened grains, whereas the magnification at 10.03 kx in Fig.2b & fig 2d the Fe₂O₃ nanoparticles showed uniformly distributed small spherical shaped particles. The figure 11a shows the sample without heating at a temperature of 400C this presents an irregular shape of the nanoparticles, while figs 11b,11c and 11d show Fe₂O₃ with a temperature of 400C for ageing 2hrs,4hrs and 6hrs respectively, these nanoparticles have a more regular basis.

The crystalline grain size is mainly determined by both the formation energy of growth unit and the lattice energy, besides different synthesis conditions. In the present study, Fe₂O₃ nanoparticles were synthesized by varying ageing time, the mass

ratio of FeCl_3 and urea, and so forth. Figure 2a shows the SEM image of the synthesized $\gamma\text{-Fe}_2\text{O}_3$, confirming that the particles obtained were indeed in the nanometre range. Upon ageing for different durations, it was observed that the grain size decreased with increasing ageing time. The smallest grain size (nm) was obtained after ageing for 6 hours. SEM analysis was used to confirm the morphology of the synthesized iron oxide sample (Figure 2). The obtained results using scanning electron microscopy analysis clearly show that the IO-NPs have spherical shape. The nanoparticles size was roughly estimated to be about 60 – 70nm. SEM images also clearly showed the nanostructural homogeneities and remarkably unique neck-structured morphology with average size of 50 – 60nm. Further study is needed to clarify the mechanism.

The CV profile shows two anodic peaks, one during the positive going potential and other during the negative going potential known as forward oxidation peak and reverse oxidation peak respectively. The forward oxidation peak is obtained due to the oxidation of methanol which forms carbon monoxide along with HCHO, HCOOH etc., which are further oxidized by adsorbed OH free radicals to CO_2 which results in the formation of second oxidation peak.

Generally the peak current density of the forward peak should be higher than that of the reverse peak which indicates that methanol oxidation is favoured over the catalyst used.

The peak current potential, peak current densities and the ratio of I_f/I_b determines the nature of methanol oxidation.

Fig.3a shows the cyclic voltammogram of the catalyst in 0.5M sulphuric acid medium.

Fig.3b shows the cyclic voltammogram of 1M Methanol oxidation over glassy carbon electrode coated with Pt- Fe_2O_3 (untreated) in nitrogen atmosphere at the scan rate of 0.1V/s at 25°C in the presence of 0.5 M H_2SO_4 which acts as supporting electrolyte as well as maintain acidic medium for methanol oxidation.

From Fig.3c. it is seen that the forward oxidation potential appears at 0.9V and reverse peak appears at 0.666V, while the current densities were found to be 0.25714 mA cm^{-2} and 0.0714 mA cm^{-2} respectively. The ratio I_f/I_b was found to be 3.601. This observation shows that methanol oxidation is highly favoured over Pt- Fe_2O_3 .

In order to understand the effect of temperature of iron oxide nano particle on oxidation kinetics, the iron oxide nanoparticles are heated to 400°C for 2hrs, 4hrs and then 6 hrs. Figs.3b-3e show the individual CV profiles and Fig. 3f shows the comparative CV of methanol oxidation of catalyst heated to 400°C for 2hrs, 4hrs and 6 hrs. The CV parameters are extracted and tabulated in Table1.

From the table, it is clearly seen that the peak current ratio gets reduced from 3.601 to 1.3387. This shows that methanol oxidation is favourable with untreated iron oxide nano particle compared to the particles heated to 400°C for 2hrs, 4hrs and 6 hrs.

5.Summary

Nano crystalline α - and γ -iron oxides were synthesized by co-precipitation method. The synthesized precursor samples were calcined at 400°C with ageing of 2hrs, 4hrs and 6hrs respectively. With increase in calcination temperature, average crystalline size and lattice parameters increased. Scanning electron micrographs clearly showed that with the increase in calcination temperature, agglomeration decreased. From SEM images, it was found that the size of the nanoparticles decreases as the amount of ageing time increases. The average size of the nanoparticles is estimated to be 50-200 nm, and 40-100 nm respectively. According to Liang et al, the influence of temperature on the synthesis of Fe₃O₄ nanoparticles is also significant. It is reported that an increase in the temperature or increased time duration of the synthetic system influences the phase of product. The CV plots for the Fe₂O₃ nanocomposite electrodes in 1M H₂SO₄ are illustrated in Figs. 3a, 3b...3f, respectively. The analysis is conducted at a constant scan rate of 10mVs⁻¹. It is worth to note that the characteristic symmetrical CV curves are generally not being observed, The deviation of the samples from exhibiting the perfect rectangular voltammograms is believed to arise from the substantial contribution of pseudocapacitance contribution to the system. From the voltammograms, it can be clearly observed that the current response of the Fe₂O₃ electrodes in 1M H₂SO₄ electrolyte is greater than the other composite electrodes, implies the most superior capacitive performance is achieved for such composition.

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