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Synthesis and Characterization of Transition Metal Oxide Nanoparticles and Their Application as Heat Transfer Fluids

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Abstract: *Objective of the study was to synthesize and characterize transition metal oxide nanoparticles (iron oxide, nickel oxide, copper oxide) and to examine their efficiency as Heat transfer fluids. Metallic oxide nanoparticles (Nickel oxide, ferric oxide, copper oxide)have been rapidly synthesized by precipitation method using ammonia as precipitating agent and are characterized by X-ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA/DSC), UV-Visible absorption (UV), Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). SEM and XRD data confirmed the formation of nanosized metal oxides. TGA verifies that the synthesized nanoparticles were thermally stable upto 1000 °C. Metallic oxide nanoparticles coupled with different base fluids such as water, mobile oil and engine oil showed better rate of heat transfer and heat discharge, indicating their potent applicability as an ingredient of nano fluids.*

1. INTRODUCTION

With the advent of nanotechnology over the last two decades transition metal oxide nanoparticles have gained considerable attention due to their wide application in various fields starting from semiconductor devices, magnetic materials, storage batteries and medicinal purpose [1-6]. Recently transition metal oxide nanoparticles have found a new application as a component for heat transfer fluid [7-8]. Where, they are mixed with the normal high energy heat transfer fluids like mobile oil, engine oil and these nano fluids are found to work with higher efficiency and better heat transfer properties. Here, in this article we report the synthesis and characterization of Iron (III) oxide (Fe_2O_3), Nickel oxide (NiO) and Cupric oxide (CuO) nanoparticles and their influence on the rate of heat transfer and rate of heat discharge of mobile oil and engine oil. Our study revealed that truly nano-sized, crystalline transition metal oxide nanoparticles were synthesized (that were characterized by UV-Visible spectroscopy, Fourier transform Infrared (FTIR) spectroscopy, X-Ray dIffractometry, Scanning Electron Microscopy (SEM) and Thermal Gravimetric Analysis (TGA)). These nanoparticles mixed with mobile oil and engine oil in different concentrations exhibited better rate of heat transfer and heat discharge. Showing promises for becoming potential ingredients of heat transfer fluids

2. MATERIALS AND METHOD:

2.1 REQUIREMENTS:

- Chemicals such as compound salt precursor and reducing agent were purchased from CDH chemicals used as such without further purifications.
- Freshly prepared conductivity water was used for preparing aqueous solutions.
- Ethanol was used for washing of precipitates.

2.2. SYNTHESIS OF NANOPARTICLES:

CuO, NiO and Fe_2O_3 nanoparticles were synthesized from their congener salts copper sulphatepentahydrate ($CuSO_4$, $5H_2O$), Ferrous Sulphateheptahydrate ($FeSO_4$, $7H_2O$) and nickel chloride hexahydrate ($NiCl_2$, $6H_2O$) respectively as starting material by aqueous precipitation method by using NH_3 as precipitating agent. 5.0 grams of each of these salts were dissolved in distill water to make a clearly solution. Then the solutions were heated up to 60^0 to 70^0C with continuous stirring using a magnetic stirring for 1 hr. after that slowly liquor ammonia solution was added from a burette to the reaction mixture at a rate 0f 0.2ml/minute with simultaneous stirring and heating. After the complete addition of liquor NH_3, the solution was filtered and the residue was washed repeatedly with acetone followed by distill water, then dried at a hot air oven at 100^0C. Finally the dried residue was calcinated at a muffle furnace at 400^0C for 3 hours. The fine coloured powder of metallic oxide nanoparticles (black colour for CuO, brown Fe_2O_3 and black NiO) were obtained as the end product.

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2.3. CHARACTERIZATION OF NANOPARTICLES:

2.3.1. UV-VIS SPECTROSCOPY:

To check the formation metallic oxide nanoparticles and their optical properties samples were analyzed by a Jasco UV-Vis spectrophotometer operated at 1 nm resolution from 300 nm to 900 nm at room temperature.

2.3.2. X-RAY DIFFRACTION MEASUREMENTS (XRD):

For the XRD measurements, the metallic oxide nanoparticle powders were sonicated using a probe-type sonicator for 15 min to avoid any possible agglomeration. XRD measurements were done using a MODEL- ULTIMA-III RIGAKU MAKE (JAPAN) X-ray diffractometer with a Cu target slit 10 mm and using a Cu Kα radiation of 1.54 Å wavelength. Scanning was done in a rate of $0.02^{\circ}min^{-1}$ in the region of 10° to 90° with a time constant of 2 min.

2.3.3. FTIR SPECTROSCOPY:

For the FTIR analysis the metallic oxide samples were dried and grinded with KBr pellets and analyzed on a Nicolet IR 200 (Thermo Electron Corp).

2.3.4. THERMAL GRAVIMETRIC ANALYSIS (TGA) AND DIFFERENTIAL THERMAL ANALYSIS (DTA):

The thermal gravimetric studies were done using a Pyris Diamond TG/DTA of PerkinElmer (Singapore) operating at a Nitrogen atmosphere (150 ml min^{-1}). Platinum crucible was used with alpha alumina powder as reference.

2.3.5. SCANNING ELECTRON MICROSCOPY OF METALLIC OXIDE NANOPARTICLES:

A droplet of solution of metallic oxide nanoparticle suspension was transferred on a clean glass slide (1 cm X 1 cm) and micrographs were taken at a number of random locations with the help of Carl Zeiss SEM at an accelerating voltage of 15 KV after gold coating.

2.4 MEASUREMENT OF RATE OF HEAT TRANSFER AND DISCHARGE OF METALLIC NANO OXIDES AS INGREDIENTS OF NANO FLUID

Mobile oil and engine oil was taken as the base fluids.Fe_2O_3, NiO and CuO nanoparticles were added to them separately at various concentrations (5mg/ml, 10 mg/ml and 15mg/ml). These solutions were heated from 0°C to 100°C in a water bath using an isolated chamber. The rate of rise in temperature and rate of heat discharge once heated was monitored using a calibrated mercury thermometer.

3. RESULTS AND DISCUSSION

3.1 UV-VISIBLE SPECTROSCOPY:

Surface Plasmon Resonance (SPR) is observed in metallic nanoparticles due to the close proximity of valence band and conduction band that allows the free movement of electrons [9, 10]. The phenomenon arises due to the resonance of the collective oscillation frequency of the free moving electrons to that of incident light [10]. It has been proved that with decrease in size of NPs, the SPR peak of their UV-Vis spectrum shifts to shorter wavelength [11-12].

The UV spectrum of Fe_2O_3 exhibited an absorption peak at 601nm, whereas the NiO and CuO nanoparticles showed the absorption peaks at 352 nm and 315 nm respectively (Fig1), which are in good accordance with earlier literature values [13-15].

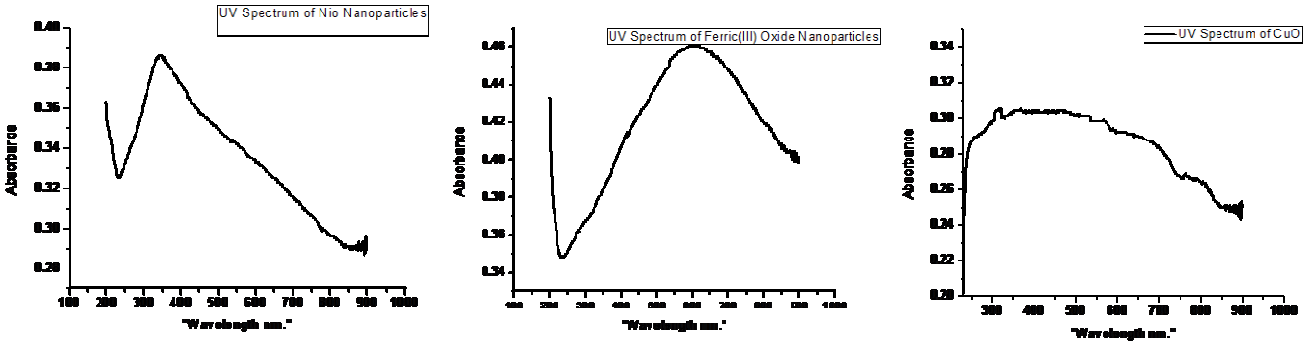

Fig. 1. UV spectrum of a)NiO, b) Fe_2O_3 and c) CuO nanoparticles

3.2. FOURIER TRANSFORMATION INFRARED SPECTROSCOPY (FTIR):

FTIR spectrum of Fe_2O_3 nanoparticles shows a very strong peak at 538 cm^{-1} suggesting Fe-O bond stretching [15]. FTIR spectrum of NiO nanoparticle exhibits a very strong peak at $477cm^{-1}$ depicting Ni-O bond vibration similar to earlier reports [16]. Both of these spectra did not show any peaks due to O-H and N-H stretching suggesting that calcination at very high temperatures have removed all the traces of adsorbed H_2O and NH_3. However, the FTIR spectrum of CuO nanoparticles exhibit multiple peaks at

3569cm^{-1}, 3380 cm^{-1}, 1062 cm^{-1}, 860 cm^{-1}, 584 cm^{-1} and 460 cm^{-1} respectively (Fig 2c).The peaks at 3569 and 3380 cm^{-1} are attributed to O-H and N-H stretching due to adsorbed H_2O and NH_3, the peak at 860cm^{-1} is due to Cu-O-Cu vibration whereas the peaks at 584 cm^{-1} and 460 cm^{-1} are due to characteristic Cu-O stretching vibration [17]

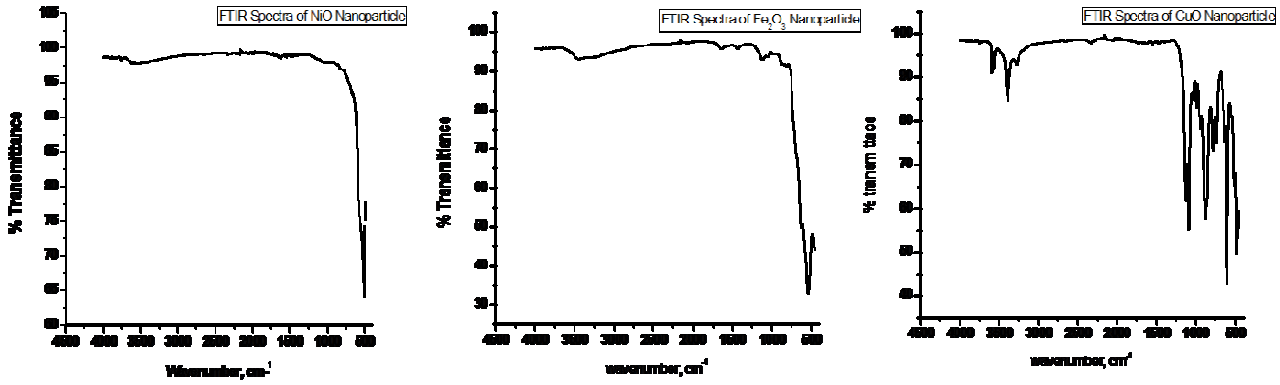

Fig. 2. FTIR spectra of a) NiO b) Fe_2O_3 and c) CuO nanoparticles

3.3. X-RAY DIFFRACTION ANALYSIS (XRD):

XRD pattern of Fe_2O_3 nanoparticles suggest formation of crystalline nanoparticles with peaks at 2θ values 35.625^0 (110), 57.668^0(121) and 63.389^0(130) respectively. Planes corresponding to those peaks (given in parenthesis) were assigned according to JCPDS Card No 85-0987. X-ray spectra of NiO nanoparticles shows peaks at 2θ values at 37.389^0 (111), 43.480^0 (200) and 62.915^0(220) as per the JCPDS Card No 68-0643. The XRD profile of CuO nanoparticles showed peaks at 32.68^0 (110), 35.923^0(111), 38.937^0(200), 49.191^{0}2(112), 53.826^0(020), 58.827^0(202), 61.682^0 (113), 67.117^0 (311), 68.328^0(221), 72.552^0(311) and 75.361^0(004) according to JCSPDS Card No-74-1021.All the diffraction peaks were assigned to certain crystalline planes, indicating absence of any impure or amorphous phases. The average particle size was calculated using the Debye-Scherer formula D=0.9λ/βcos θ [18](λ is the wavelength of radiation, θ is the angle and β is the full width of the absorption peak at half maximum). Using this equation the particle size of Fe_2O_3 nanoparticles was calculated to be around 29nm, whereas the average particle size was calculated to be 39nm and that CuO was found to be about 66nm.

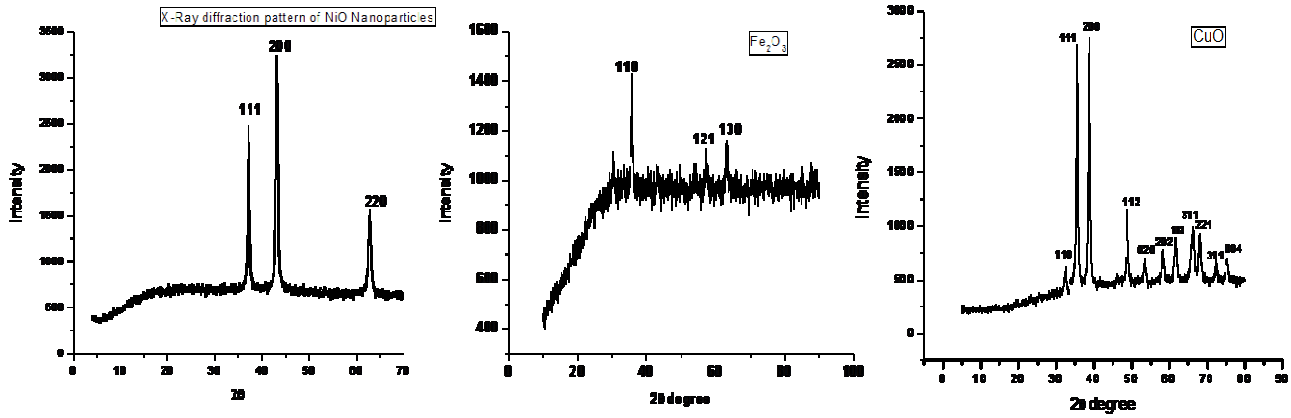

Fig. 3. XRD profile of a) NiO b) Fe_2O_3 and c) CuO nanoparticles

3.4. SCANNING ELECTRON MICROSCOPY (SEM):

From the SEM micrographs it was revealed that the actual size of the Fe_2O_3 nanoparticles was on average 66nm, somewhat higher than the XRD results probably due to the partial non-crystalline population. SEM micrographs of NiO nanoparticles showed an average diameter of 48 nm that is in good collaboration with XRD data. CuO nanoparticles showed an average diameter of about 86 nm again somewhat higher than the crystalline size calculated higher than XRD value.

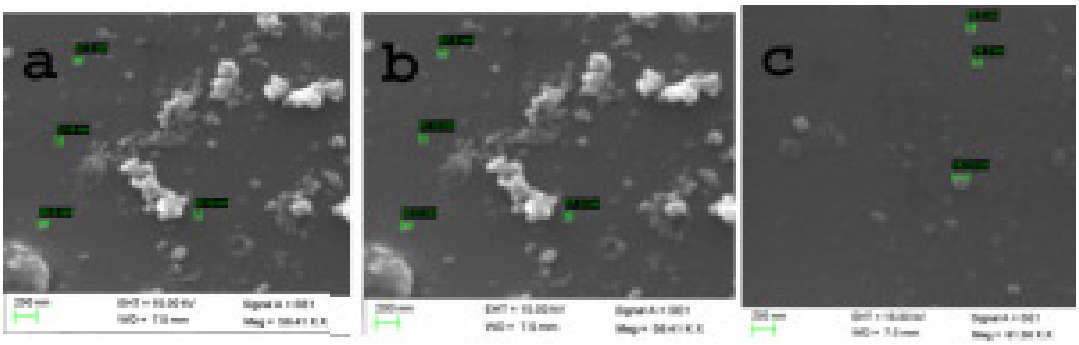

Fig. 4. SEM micrographs of a)Fe_2O_3b) NiO and c) CuO nanoparticles

3.5. THERMOGRAVIMETRIC (TGA/DSC) ANALYSIS:

Thermal gravimetric analysis was carried out from room temperature to 900°C for the metallic oxide nanoparticles. TGA plots for Fe_2O_3 and NiO nanoparticles showed that they were exceptionally thermostable as they did not show any appreciable weight loss up to 900°C. The initial endothermic peak in the DSC curve around 100°C might be attributed to the evaporation of adsorbed NH_3 and H_2O. However, the TGA plot of CuO nanoparticles show about 10% weight loss at 400°C and about 15% weight loss at 700°C, corresponding DSC curve also denotes two sharp endothermic peaks at those temperatures probably referring to the possible phase transitions.

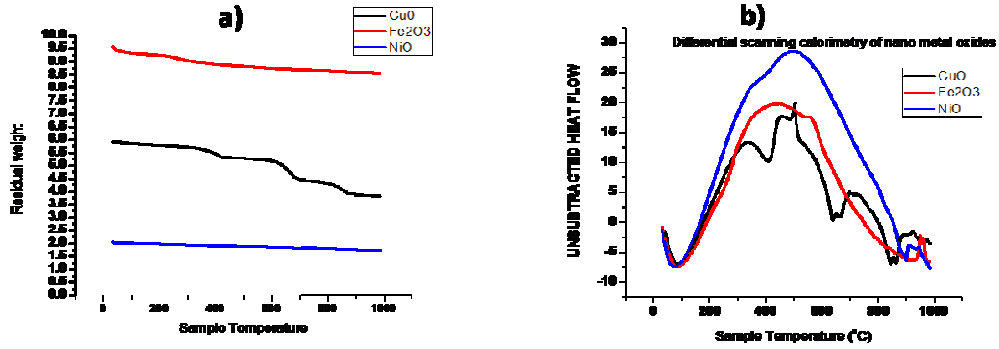

Fig.5. a) TGA and b) DSC plots of Fe_2O_3 (red), NiO (blue) and CuO (black) nanoparticles

3.6 HEAT TRANSFER PERFORMANCES OF METALLIC OXIDE NANOPARTICLES:

Heat transfer properties of the metallic nano oxides were measured by mixing them to mobile oil and engine oil as base fluids. From the measurement of rate of heat transfer and rate of heat discharge it appeared that **Fe_2O_3**nanoparticles showed the highest rate of heat transfer and slowest rate of heat discharge when mixed with mobile oil and engine oil. Other nanoparticles also enhanced the heat transfer properties of the base fluid, but as described the effect was most pronounced in case of **Fe_2O_3**nanoparticles (Fig 6 a & b).

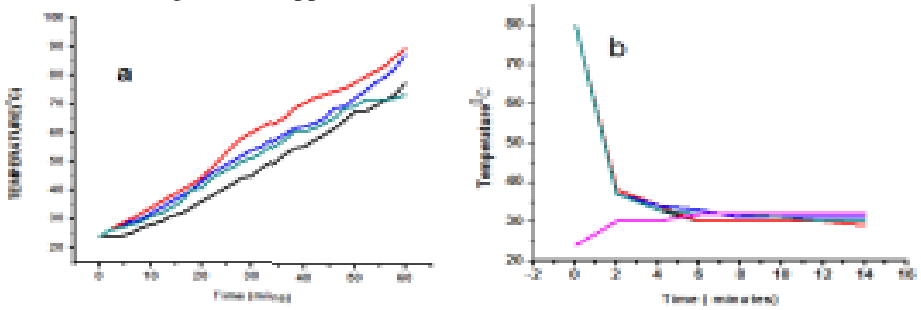

Fig. 6. (a) Rate of heat transfer with metallic nano oxides with mobile oil (Fe_2O_3 (red), NiO (blue) and CuO (black)) b) rate of heat discharge of mobile oil with metallic nano oxides(Fe_2O_3 (red), NiO (blue) and CuO (black), pink line denotes the rise in temperature of reservoir water due to discharging of nano fluids)

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5. CONCLUSIONS

Results obtained from characterization of different synthesized nanoparticles in the present study are in good agreement with the previous reports. Nano sized crystalline transition metal oxide particles were prepared successfully. The shape, size and chemical state of the synthesized powders were structurally characterized by TGA/DSC, SEM, XRD, FTIR and UV–Vis spectral techniques. Thermal behavior of prepared nanoparticles has been studied which extended their application as heat transfer fluid. Nanoparticles of iron oxide and copper oxide have good stability and heat transfer performances. From the experimental analysis it was concluded that, as the concentration of nanoparticles in the base fluid increases, it starts to behave as better heat transfer fluid.

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