CHAPTER-II

Materials, Methods and Instrumental Techniques for Physico-Chemical Studies
2.1.1 Materials

The chemicals and solvents used for the present work were of analytical grade quality. The sources of chemicals and solvents are as follows: E. Merck (India) Limited, Sigma-Aldrich (India), Lancaster (India), Spectrochem (India), s. d. fine-chem ltd., Qualigens Fine Chemicals, Central Drug House (P) Ltd., Loba Chemie Industries, Sisco Research Laboratories Pvt. Ltd. All reactants and reagents used were high-purity commercially available CoCl$_2$.6H$_2$O (99%), FeCl$_3$ (99%), KOH (96%), NaOH (96%), NaCl (99.5%), polyethylene glycol (PEG-400) (99%), ethanol (99.99%) and Pd (OAc)$_2$ were used as received. All the solvents used were of reagent grade and distilled prior to use.

2.1.2 Methods of Magnetic Nanoparticle Synthesis

(A) Synthesis of Cobalt Ferrite Magnetic Nanoparticles

(CoFe$_2$O$_4$ MNPs)

The synthesis was carried out by a wet-chemical process. The cobalt ferrite magnetic nanoparticles were sonochemically co-precipitated from the mixture Co (II) and Fe (III) salt solution at strong alkaline pH (11-12). Herein, two aqueous solutions of
CoCl\(_2\).6H\(_2\)O and FeCl\(_3\) in 1:2 mol ratios were mixed and then to this, an aqueous KOH solution was added drop-wise in an inert atmosphere under vigorous ultrasonic treatment. After complete addition of KOH, the reaction temperature was increased up to 60-70 °C and sonicated for half an hour. The black particles of CoFe\(_2\)O\(_4\) particles were observed and separated by centrifugation. The process of centrifugation (14000 rpm) and ultra-sonication was repeated till complete dispersion of the black particles. Then the particles were separated, washed, dried and kept overnight in an incubator for ageing. The particles were further dried under vacuum and dispersed in dry ethanol by sonication to obtain stable brown coloured dispersion. Fig. 2.1.1 shows CoFe\(_2\)O\(_4\) MNPs: (a) powder, (b) in ethanol without dispersion and (c) dispersion in ethanol by ultrasonication. The detailed synthesis protocol is described in Chapter 3, Section I.
Prior to incorporation of palladium into CoFe$_2$O$_4$ MNPs, palladium nanoparticles (Pd NPs) were synthesized. Then the Pd NPs were incorporated into CoFe$_2$O$_4$ MNPs during their synthesis by ultrasonication assisted co-precipitation method.

(i) **Synthesis of Pd nanoparticles (Pd NPs)**

Pd NPs with narrow size distribution were synthesized following the method reported by Wang et al. [1]. 0.05 g of $2.2 \times 10^{-4}$ M Pd(OAc)$_2$ was added into 4 g of $2.0 \times 10^{-3}$ M polyethyleneglycol (PEG-400) (Fig.2.1.2.a). The reaction mixture was then stirred in a magnetic stirrer at 80 °C for 1 h. The resulting light yellow homogeneous solution was further stirred for 2 h at the same temperature during which the color of the solution slowly turned from light yellow to gray dark, indicating the formation of Pd NPs. The as-synthesized PEG stabilized Pd NPs was then solidified by cooling at room temperature. The Pd NPs were then dispersed in dry ethanol by sonication (Fig. 2.1.2.b). The dispersion was further centrifuged at 14000 rpm at 10 °C and the separated particles were washed properly with ethanol. The particles were dried under vacuum and preserved for further use.
(ii) Synthesis of Pd incorporated CoFe$_2$O$_4$ NPs (Pd-CoFe$_2$O$_4$ MNPs)

CoFe$_2$O$_4$ NPs were synthesized by a combined sonochemical and co-precipitation technique. For this, two aqueous solutions of FeCl$_3$ (9.3 mmol, 50 mL) and CoCl$_2$.6H$_2$O (4.2 mmol, 50 mL) in distilled de-ionized water were mixed in a 200 mL flat bottom flask and placed in an ultrasonic bath. An aqueous NaOH solution (3M, 25 mL) was added drop-wise under argon atmosphere with continuous ultrasonic irradiation (frequency 40 KHz and power of 40 KW). Prior to mixing, all these three solutions were sonicated for 30 min to remove dissolved oxygen. The temperature of the sonicator bath was raised up to 60 °C and the mixture was further sonicated for 30 min. in air atmosphere. The black precipitate formation was observed during that time. To the reaction mixture, was then added the dispersion of Pd NPs in ethanol and the reaction temperature was slowly brought to 80°C. The mixture was further kept under sonication for 1 h and then slowly cooled down to room temperature. The black precipitate was then separated by centrifugation at 15000 rpm for 15 min., washed several times with both distilled water and ethanol and kept overnight in an incubator at 60 °C. The precipitate was then further dried in an oven at 100 °C for nearly an hour and subsequently kept in highly evacuated environment (10$^{-2}$ bar) for another 1 h. At this stage the product (Pd doped CoFe$_2$O$_4$) contains some associated water which was then removed by heating the product at 200 °C for 6 h. Fig. 2.1.3 shows Pd-CoFe$_2$O$_4$ MNPs: (a) powder and (b) dispersion in ethanol by ultrasonication.
Fig. 2.1.2 (a) Pd (II) acetate in PEG-400 and (b) Pd NPs in ethanol

Fig. 2.1.3 Pd-CoFe$_2$O$_4$ (a) powder and (b) dispersion in ethanol by sonication
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Instrumental Techniques for Physico-Chemical Studies

Characterization of the magnetic nanoparticles was performed using the following techniques:

2.2.1 Scanning Electron Microscopy (SEM)

The synthesized ferrite magnetic nanoparticles were first characterized by scanning electron microscopy. A Zeiss LEO 1430VP type SEM was used to observe the morphology and the size distribution of the nanoparticles. The samples were dispersed in ethanol and deposited on aluminum sample stubs using sticky carbon tabs and dried in air. Then the sample surfaces were made conductive by coating with a thin layer of Au/Pd in a sputter coater unit (Polaron, SC 1742). The samples were scanned by electron beam at an accelerating voltage of 10-15 kV keeping the working distance of 15 mm using secondary electron detector. A filed emission scanning electron microscope (FESEM) (Zeiss, Sigma) was also used to observe the surface morphology at very high magnification and resolution. Fig.2.2.1 shows the (a) photographic view and (b) schematic diagram of a SEM instrument.
2.2.2 Transmission Electron Microscopy (TEM)

The shape and size of the magnetic nanoparticles was determined using a 200 kV TEM (JEOL JEM2100, Japan) with the potential of performing selected-area electron diffraction (SAED). For TEM measurement, a drop of nanoparticles dispersed in solvent was placed on a carbon coated copper grid (400 mesh size) and allowed to dry in air. The nanoparticles were observed at bright field TEM images at the magnifications of 20 to 300 KX. The crystalline nature of the nanoparticles was further investigated by high resolution TEM (HRTEM) and SAED pattern. The photographic view and the cut view of a typical TEM instrument is shown in Fig. 2.2.2.
2.2.3 X-ray Diffraction (XRD)

X-ray diffraction (XRD) technique allows identification of various crystalline phases present in the material and provides other structural information such as the average size of the crystallites, strains present inside the crystallites etc.

The structure and crystallite size of the nanoparticles was determined by XRD, using a Bruker AXD D8 diffractometer with Cu Kα radiation (\(\lambda = 1.54178 \text{ Å}\)) and graphite monochromator from 10° to 80° (2\(\theta\)) at a scanning rate 5 °/min. Samples were taken in powder form for the measurement except in few cases the samples were deposited on glass substrate. The working voltage was 40 kV and the current was 40 mA. The crystalline size was calculated from line broadening of the maximum intense...
XRD-peak by Scherrer’s formula, where the Scherrer constant (particle shape factor) was taken as 0.9.

2.2.4 Vibrating Sample Magnetometer (VSM)

Magnetic properties of the magnetic nanoparticles, such as saturation magnetization, coercivity, and remanence were measured in a Lakeshore 7410 vibrating sample magnetometer. In order to eliminate the interaction of the particles in the samples, the powder was dispersed in paraffin. For the measurement, 0.02 g of the sample weight was fixed to the tip of the vibrating rod and analyzed at variable temperatures. Fig. 2.2.3 depicts a photographic view of VSM.

![Photographic view of a vibrating sample magnetometer](Lakeshore Model 7410)

**Fig. 2.2.3** Photographic view of a vibrating sample magnetometer (Lakeshore Model 7410)
2.2.5 Fourier Transform Infrared (FTIR) and Raman Spectroscopy

FT-IR spectra were collected in the range from 400 to 4000 cm\(^{-1}\), using Perkin Elmer Spectrum One FT-IR spectrophotometer on KBr pellets. The spectra revealed the characteristic metal-oxygen bonds and the surface functionalities of ferrite nanoparticles.

The Raman spectra of as-synthesized CoFe\(_2\)O\(_4\)-ZnS and ZnS NPs were recorded using 633 nm line of He-Ne laser as excitation source in a Laser Micro-Raman Spectrometer (HORIBA Jobin Yvon, Lab RAM HR) at room temperature.

2.2.6 Elemental analysis

Oxford's EDX (Energy Dispersive X-ray) detector equipped with the SEM and TEM was used for studying the elemental composition of samples.

2.2.7 Surface area analysis

The specific surface area and the adsorption isotherm curve of magnetic nanoparticles were measured with a COULTER SA 3100 analyzer using the multipoint Brunauer, Emmett, and Teller (BET) adsorption. The samples were first out-gassed for 2 h at 200 °C in vacuum and then analyzed by the Backman Coulter Surface Area and Pore Size Analyzer at liquid nitrogen temperature (-196 °C).
2.2.8 Other Spectroscopic measurement

The absorption spectra of nanoparticles and photocatalytic activity of CoFe$_2$O$_4$-Cr$_2$O$_3$ and CoFe$_2$O$_4$-ZnS nanocomposites were evaluated by a UV-VIS Spectrometer (Cary 50 Bio, Varian).

The fluorescent properties nanoparticles were measured in the time-resolved steady state photoluminescence spectrometer (Eddinburg FSP920).

The ESR spectra were recorded using a JEOL JES FA200 ESR spectrometer at variable temperatures.

Characterization of organic compounds

Characterization and structural assessment of various products in organic transformations and the newly synthesized compounds were performed by FT-IR, NMR (Varian 400 MHz FT-NMR), LCMS (Waters Q-Tof Premier) and single crystal XRD (Bruker Nonius Smart Apex II X-ray Single crystal diffractometer) analysis.

2.2.9 References