One pot facile synthesis of nanosized Iron (III) oxide by direct precipitation method

Dr. Ritu
Department of chemistry, Chhotu Ram Arya Collage, Sonepat-131001 (Haryana)

Received: May 05, 2018 Accepted: June 19, 2018

ABSTRACT *Nanosized metal oxide namely iron oxide has been synthesized by precipitation method and characterized by using XRD (X-ray diffraction), TEM (transmission electron microscopy) and Magnetic Measurements techniques. XRD studies show that iron oxide was formed as α- Fe_2O_3 instead of the commonly formed magnetite nanoparticles (Fe_3O_4) or a mixture of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3, cubic) and it has rhombohedral structure. Magnetic measurements showed iron oxide has five unpaired electrons and is paramagnetic in nature. The particle size of the synthesized iron oxide was determined by TEM. TEM images show that the size of particles of Fe_2O_3 varied from 15nm to 42nm which is in good agreement of the theoretically predicted size of nanomaterials. This method is convenient, easy and effective in comparison to the known methods of the synthesis of nanomaterials like thermal decomposition of precursors, co-implantation of metal and oxygen ions and ultrasonic spray pyrolysis.*

Keywords: *Nanomaterial, iron oxide, TEM, metal oxides, XRD analysis*

1. Introduction:

Transition metal oxides have many applications as catalyst [Xu et al., 2003; Wei-zhong et al., 2008; Hsin-Chun et al., 2008; Altinçekiç et al., 2008, Bennici et al., 2003], sensors [Yang et al., 2011; Wei et al., 2010, Guimin et al., 2008; Sharma et al., 1999], superconductors [Pillai et al., 1995; Wu et al., 2003] and adsorbents [Zou et al., 2006; Runping, 2009]. Iron oxides belong to the most abundant minerals and occur with a large variety of stoichiometries, structures, and properties. The more important ones are FeO (wustite), λ-Fe_2O_3 (maghemite), α-Fe_2O_3 (hematite), and Fe_3O_4 (magnetite) with rock-salt, vacancy rich inverse spinel, corundum, and inverse spinel structures, respectively; the two former ones being thermodynamically less favorable and α-Fe_2O_3 being the most oxidized one. Iron oxides are widely used in industry as catalysts or catalyst supports. Metal-oxides constitute an important class of materials that are involved in environmental science, electrochemistry, biology, chemical sensors, magnetism and other fields. One of their most important applications is heterogeneous catalysis. Heterogeneous catalysts based on magnetic mixed iron oxides (MO-Fe_2O_3; M: Fe, Co, Cu, Mn) were used for the decolorization of several synthetic dyes like bromophenol blue, chicago sky blue, Cu-phthalocyanine, eosin yellowish, evans blue, naphthol blue black, phenol red, poly B-411, and reactive orange 16. All the catalysts decomposed H_2O_2 yielding highly reactive hydroxyl radicals, and were able to decolorize the synthetic dyes. The most effective catalyst FeO-Fe_2O_3 (25 mg mL^{-1} with 100 mmol L^{-1} H_2O_2) produced more than 90% decolorization of 50 mg L^{-1}bromophenol blue, chicago sky blue, evans blue and naphthol blue black within 24 h [Baldrin et al, 2006]. Aluminium stabilized mixed metal oxide of copper and iron serve as an active catalyst for the nitration of benzene in solid–liquid phase reaction, using 69% nitric acid as a nitrating agent. The reaction was carried out with 100% selectivity towards nitro benzene [Chaubal & Sawant., 2006]. Titania- and iron oxide-supported gold catalysts have been used for the hydrogenation of propyne [Lopez-Sanchez & David 2005]. Fe_2O_3, Mn_2O_3, and calcined physical mixtures of both ferric and manganese oxides with alumina and/or silica gel have been used for the catalytic dehydration of ethanol [Zaki 2005]. The catalytic behaviour of α-Fe_2O_3-based catalysts has been investigated for the toluene ammoxidation reaction [Rombi, et al., 2004]. Iron (III) hydroxide has been used for the photooxidation of 2-aminophenol in aqueous solution [Andreozzi et al., 2003]. The partial oxidation of propane to formaldehyde using uranium mixed oxide catalysts has been performed. Outstanding results for the selective oxidation of propane and propene to formaldehyde were obtained using Fe/U catalysts [Taylor, et al, 2003]. An efficient and selective acylation of alcohols and amines employing carboxylic acids as acylating agents has been done by the metal oxide containing activated carbon catalyst, catalyst was synthesized by carbonization of organic ion-exchangers after incorporation of Fe^{3+} ions with exchangeable cations present in resin [Sreedhar et al., 2003]. Dehydrogenation of ethylbenzene has been studied using Potassium-promoted Iron oxide as catalyst [Ketteler et al., 2002]. The sensitized photocatalytic degradation of mono-, di- and trichlorophenols with aqueous suspensions of α-Fe_2O_3 and α-FeOOH has been reported [Bandara et al., 2001]. The oxidative dehydrogenation of propane on α - Fe_2O_3 has been done in the presence and absence of tetrachloro methane at 723K [Sugiyama, et al., 2001]. Intramolecular condensation reactions of pentamethylene and

hexamethylene glycols over iron oxide has been studied [Grabowska et al., 2000]. Catalysts consisting of sodium-promoted silica gel-supported iron oxide has been found to catalyze the gas phase epoxidation of propene by nitrous oxide. Selectivity's to propene oxide of 40–60% at propene conversions in the range of 6–12% were observed [Duma & V 2000]. The catalytic conversion of benzoic acid to phenol in the presence of water and oxygen was studied in the vapor phase over nickel oxide on various supports, like iron oxide and silica [Dumaa et al., 2004]. Fine particle iron oxide based aerogels have been used as catalyst for the partial oxidation of methanol [Wang & Willey 1999]. Oxidation of benzoic acid has been studied via Fenton-like reaction using an innovative supported γ-FeOOH catalyst [Chou & Chihpin 1999]. Iron oxide and iron carbide have been used as catalyst for the dehydration of tertiary alcohols [Wang & Davis 1999]. Selective reduction of nitro groups in aromatic azo compounds has been done in the presence of an iron oxide/hydroxide catalyst [Lauwiner et al., 1999]. Reduction of aromatic nitro compounds with hydrazine hydrate in the presence of an iron oxide hydroxide catalyst has also been studied [Benz et al., 1998]. Decolorization of synthetic dyes by hydrogen peroxide with heterogeneous catalysis by mixed iron oxides [Baldrian et al., 2006]. Nanosized iron oxides have considerable attention due to their unique magnetic properties (superparamagnetism, high coercivity, low Curie temperature, high magnetic susceptibility, non-toxicity, biocompatibility and low cost of production, which allows their usage in various nanotechnology applications in a broad range of disciplines. Magnetic nanoparticles are also important in biomedical applications e.g. magnetic bioseparation [Miller and Orgel 1974], magnetic target drug delivery [Paecht et al., 1970], hyperthermia [Wang et al., 2011], magnetic resonance imaging [Chomoucka et al., 2010], magnetofection [Kumar & mohammad, 2011]. These particles have an ability to interact with various biological molecules in different ways due to their superparamagnetic properties, high specific area and wide choice of surface functionalization. In the present manuscript we have synthesized α - Fe_2O_3 nanoparticles by simple aqueous precipitation using ammonia as precipitating agent. This method involves a simple, cheap and one step process for synthesis of Fe_2O_3 nanaoparticles. The obtained particles of Fe_2O_3 have size from 60-100 nm. The synthesized nanoparticles were characterized by XRD, Magnetic susceptibility and TEM

2. Methods and materials

2.1 Chemicals:

All chemicals used in the experiment are analytic reagent grade. Ferric nitrate $Fe_2(NO_3)_2$ was purchased from Merck, India. Ammonium hydroxide (liquor ammonia) was purchased from SRL. Deionized water was used throughout the experiment.

2.2 Synthesis of iron oxide:

500 ml of 0.1M solution of $Fe_2(NO_3)_2$ was taken and aqueous ammonia was added drop wise with constant stirring until the pH of the solution reached to 10. The precipitates thus obtained were filtered by Buckner funnel and was washed several times with distilled water. The precipitates were dried in oven at 70°C for 24 hrs and were calcined at 500°C in a muffle furnace for 5 hrs. Obtained material was ground and sieved through 100 mesh size sieve.

2.3 Equipments:

The powder X-ray diffraction (XRD) was performed using X-ray diffractometer system Philips PW 11/90, with nickel filtered CuKα (l = 1.5405 Å) radiation. Magnetic measurements were done using vibrating sample Magnetometer Model 155. The transmission electron microscopy (TEM) was performed with Tecnai 20G2 under 200 KV.

Results and discussions:

3.1. X-ray studies:

X-ray diffraction of synthesized oxide is shown in Figure (1). X-ray diffraction pattern of pure iron oxide indicated that iron oxide in the form of α - Fe_2O_3 [Fig- 1]. In X-ray diffraction, some prominent peaks were considered and corresponding d-values were compared with the standard [JCPDS file No. 85-0987] [Table-1]. .X-ray diffraction shows that metal oxide is pure α - Fe_2O_3 having rhombohedral structure. Thickness of the particle size has also been calculated using Shehreer formula and it has been calculated as 28 nm to 49 nm which is in good agreement of the nanosized particle size (upto 100 nm)

3.2 Magnetic measurements:

The magnetic moment for iron oxide is found to be 5.68 B.M. This value of magnetic moment supports the fact that the formed iron oxide is in the form of Fe_2O_3 with actual magnetic moment 5.92B.M. This indicates that 5 unpaired electron is present in Fe_2O_3.

Thus the oxide formed is paramagnetic in nature. In case of iron oxide magnetic measurements were done at temperatures ranging from 300 K to 100 K to determine the temperature of Morin transition. The results are shown in Fig 2 and have been reported in Table 2.

3.3 TGA/ DTA studies:

TGA/DTA transition shows an endothermic peak at 364^0 C [Fig.3]. It simply indicates that when FeO (OH) is heated, it takes an amount of energy and 1.5 water molecules are removed. So, for the formation of iron oxide temperature above 364^{0}C is required.

3.4 Surface Area Measurement:

The specific surface area of metal oxides was determined using BET method. Surface area of the metal oxides was 27 m^2/g.

3.5 SEM/TEM studies

SEM/TEM studies were performed to find out morphology and exact particle size of synthesized Fe_2O_3. SEM/Tem images show that Fe_2O_3 nanoparticles are having particle size in the range of 15-40 nm [Fig. 4 & Fig.5].

4. Conclusion:

α - Fe_2O_3 nanoparticles with corundum structure are synthesized successfully by aqueous precipitation method. From TEM study, it is found that particles are with average size of 15-42 nm. Magnetic measurements shows that Fe_2O_3 has five unpaired electron and hence paramagnetic in nature. XRD studies show that iron oxide was formed as α- Fe_2O_3 instead of the commonly formed magnetite nanoparticles Fe_3O_4 or a mixture of magnetite and maghemite. This method is advantageous over the existing methods of synthesis of nanoparticles because other methods require specialized instrumentation, highly skilled labour, expensive materials and methods. Therefore, the proposed precipitation method is very promising and may have extensive applications for the synthesis of nanosized iron oxide particles.

Table 1

X-ray diffraction data for iron oxide (α - Fe_2O_3)

S. No.	d (A^0) (Observed)	d (A^0) (Reported)	I/I0 × 100 % (Observed)	I/I0 × 100 % (Reported)	t (nm)
1.	3.6806	3.6775	35.78	58.7	43.8
2.	2.6980	2.6959	100.00	100	44.7
3.	2.5155	2.5135	83.14	63.1	49.6
4.	2.2033	2.2015	24.03	3.4	31.1
5.	1.8394	1.8379	36.98	6.1	43.1
6.	1.6949	1.6936	43.26	18.0	43.9
7.	1.4852	1.4840	26.88	18.1	45.8
8.	1.4511	1.4512	26.77	9.7	28.3

Table 2

Magnetic susceptibility data of iron oxide

Temperature(K)	Volt(mV)	Magnetic moment(e.m.u.)
300	5.75	0.0050
290	5.58	0.0051
280	5.38	0.0052
270	5.17	0.0054
260	4.96	0.0055
250	4.75	0.0057
240	4.54	0.0060
230	4.33	0.0062
220	4.13	0.0056
200	3.71	0.0049
180	3.29	0.0045
160	2.88	0.0043
140	2.46	0.0042
120	2.05	0.0041
100	1.63	0.0040

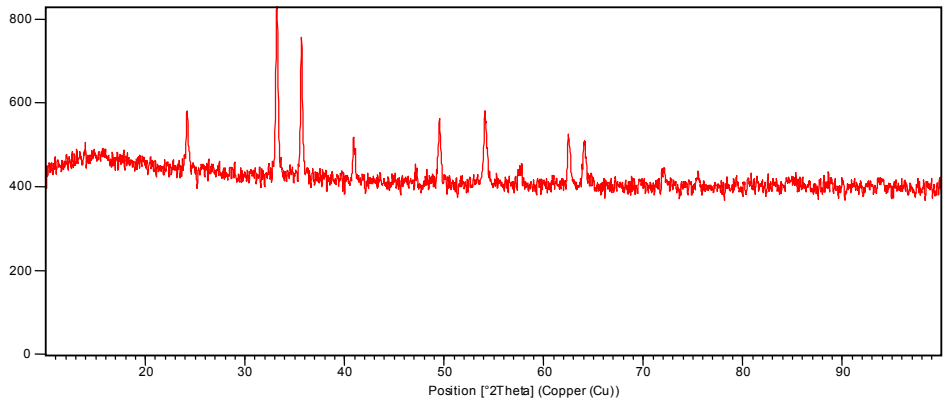


Fig.1- XRD spectra of synthesized iron oxide

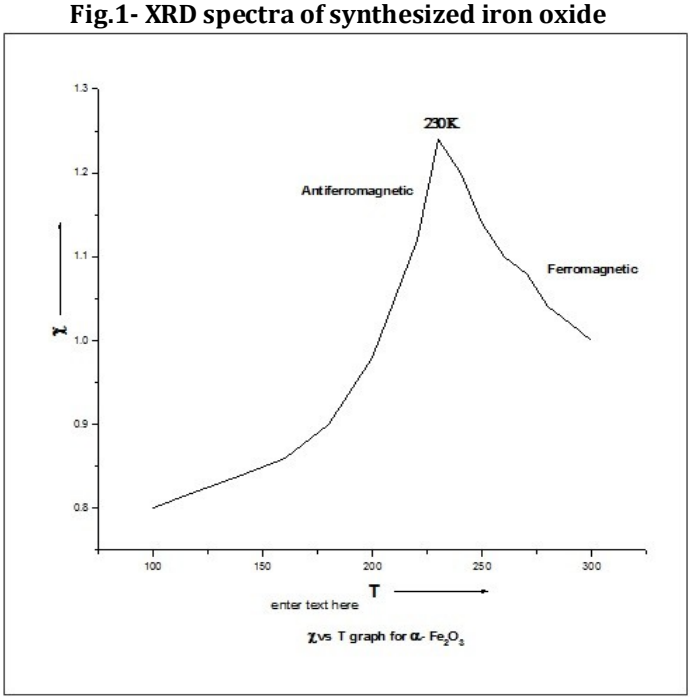


Fig.2- Magnetic measurements of synthesized iron oxide at different temperatures

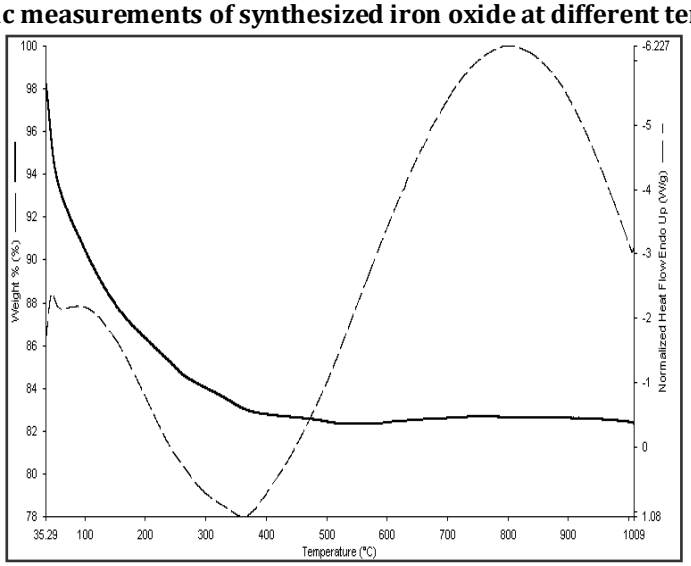


Fig.3. TGA/DTA curve of iron oxide heated at 70° C

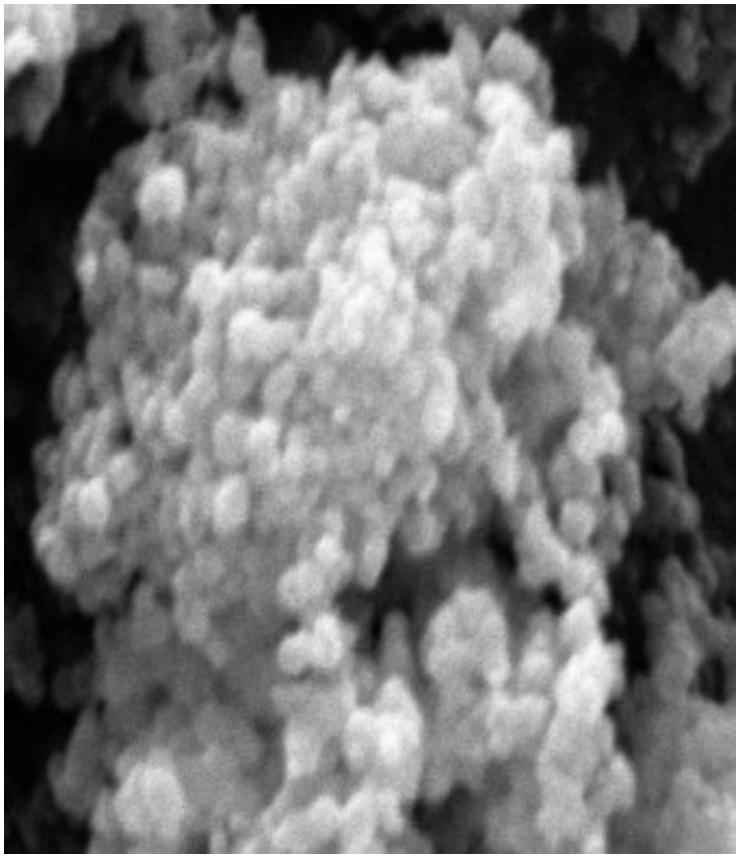
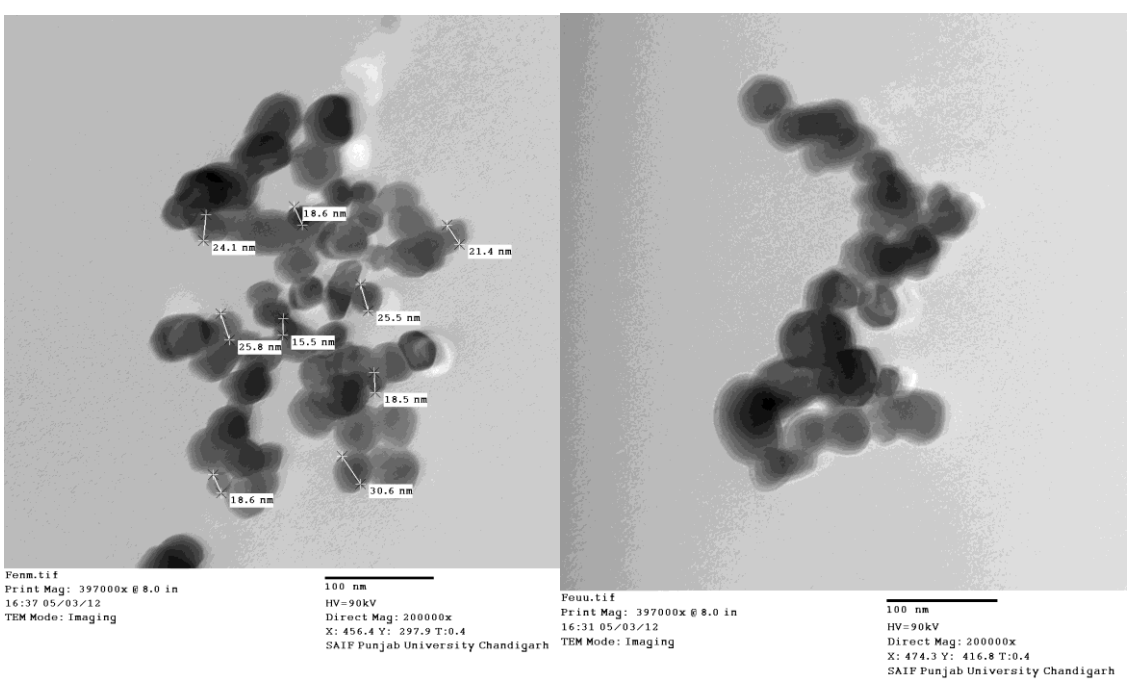


Figure 4: SEM images of iron oxide particles



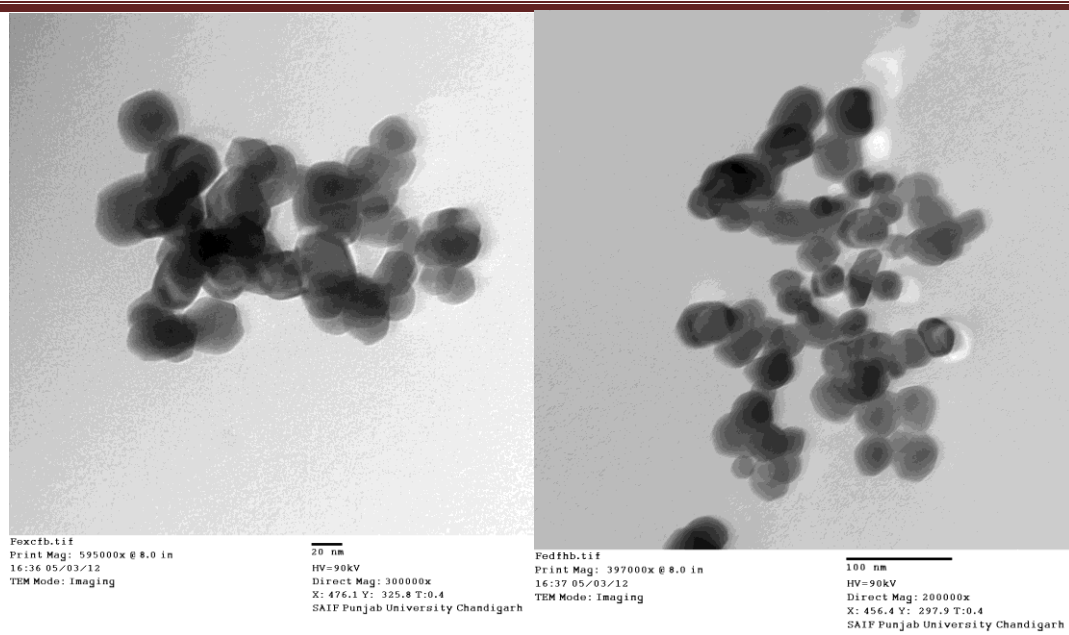


Figure 5: TEM images of iron oxide particles

References:

1) Xu, J. Z., Zhu, J. J., Wang H. and Chen, H. Y., 2003. Nano-sized iron oxide modified carbon paste electrodes as an amperometric sensor for amikacin. Anal. Lett. 36(13), 2723-2733.
2) Wei-zhong Lv, Liu, Bo, Luo, Zhong-kuan, Ren, Xiang-zhong and Zhang,, Pei-xin 2008. XRD studies on the nanosized copper ferrite powders synthesized by sonochemical method, Jr. of Alloys and Compounds. 465, 1-2, 261-264.
3) Hsin-Chun Lu, Jo-Ling Lu, Chun-Lung Chu, Chi-You Lai, Gwo-mei Wu, 2008. Preparation of Nano-Powders of p-Type Transparent Conductive Copper Aluminum Oxide by Co-Precipitation Method, 2nd international conference 2008 2nd IEEE International Nanoelectronics Conference, 485-488.
4) Altincekic, T. G., Boz, I, Aktürk, S. J., 2008. Synthesis and characterization of nanosized Cu/ZnO catalyst by polyol method, Nanosci Nanotechnol. 8(2) 874-877.
5) Bennici, S., Gervasini, A. Ragaini V., 2003. Ultrasonic sonochemistry, Preparation of highly dispersed CuO catalysts on oxide supports for de-NO(x) reactions, 10, 2, 61-64.
6) Yang, M., He, J., Hu, X., Yan, C., Cheng, Z., Zhao, Y., Zuo, G., 2011. Copper oxide nanoparticle sensors for hydrogen cyanide detection: Unprecedented selectivity and sensitivity, Surface and interface Physics papers A, 155, 2, 692-698.
7) Wei, H., Sun, H., Wang, S., Chen, G., Hou, Y., Guo, H., Ma, X., 2010. Low temperature H_2S sensor based on iron oxide/tin dioxide thick film, Jr. of Natural Gas Chemistry, 393-396.
8) Guimin, An. Yang, Z., Li-Zhimin, Zhenhang, M., Buxing, H., Shidding, M., Jianping, Li. 2008. Nanotechnology, 19, 101-103.
9) Sharma., S.S. Nomura, K. Jihira, Y.U. 1999. Characterization of tin oxide films prepared as gas sensors by conversion electron Mössbauer spectrometry, Journal of Material Science, 26, 4104-4109.
10) Pillai, V., Kumar, P., Hou, M.J. Ayyub, P., Shah, D.O., 1995. Preparation of nanoparticles of silver halides, superconductors and magnetic materials using water-in-oil microemulsions as nano-reactors Advance in colloid and Interface Science, 55, 241-269.
11) Rongcheng, Wu, Jiuhui, Qu., Hong He, Yunbo Yu, 2003. Preparation and characterization of Cu catalysts supported on organized mesoporous alumina Journal of Beijing University of chemical technology (Natural science edition), 48, 2311-2316.
12) Zou, W. R., Han, Z., Zhang, J. Shi, Hangmin, Li. 2006. Characterization and Properties of Manganese Oxide Coated Zeolite as Adsorbent for Removal of Copper(II) and Lead(II) Ions from Solution, Jr. of Chemical and Engineering data, 51, 534-541.
13) Runping, H., Lina, Z., Xin, Z., Yanfang, X., Feng, X., Yinli, L., Wang, Y. 2009. Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column, Jr. of Chemical Engineering, 149, 1, 123-131.
14) Baldrin, P., Merhautova, V., Gabriel, J., Nerud, F., Stopka, P., Hruby, M., Benes, M.J., 2006. Decolorization of synthetic dyes by hydrogen peroxide with heterogeneous catalysis by mixed iron oxides, Applied Catalysis B-Environmental 66, 258-264.

15) Chaubal, N.S., Sawant, M.R., 2006. Synergistic role of aluminium in stabilization of mixed metal oxide catalyst for the nitration of aromatic compounds, catalysis communications, 7, 443 - 449.
16) Lopez-Sanchez, J.A. David, L., 2005. The use of titania - and iron oxide - supported gold catalysts for the hydrogenation of propyne, Applied Catalysis A, 291 (1-2), 230 - 237.
17) Zaki, T., 2005. Catalytic dehydration of ethanol using transition metal oxide catalysts, Journal of Colloid and Interface Science, 284**,** 606 - 613.
18) Rombi, E., Ferino, I., Picciau, R.C., Solinas, V., Buzzoni, R., 2004. Toluene ammoxidation on α-Fe_2O_3 based catalysts, Applied Catalysis A, 266**,** 73 - 79.
19) Andreozzi, R., Vincenzo C., Raffaele M., 2003. Iron (III) hydroxide-mediated photooxidation of 2-aminophenol in aqueous solution: A kinetic study, Water Research, 37, 3682 - 3688.
20) Taylor, S.H., Hutchings, G., Palacios, JM.-L. Lee, D.F., 2003.The partial oxidation of propane to formaldehyde using uranium mixed oxide catalysts, Catalysis Today 81, 171 - 178.
21) Sreedhar, B., Bhaskar, V., Sridhar, T., Srinivas, L., K. and Klára, S, 2003. Acylation of alcohols and amines with carboxylic acids: A first report catalyzed by iron (III) oxide-containing activated carbon, Journal of Molecular Catalysis A: Chemical 191, 141 – 147.
22) Ketteler, G., Ranke, W. Schlogl, R., 2002, Potassium-promoted iron oxide model catalyst films for the dehydrogenation of ethylbenzene: An example for complex model systems, Journal of Catalysis, 212**,** 104 – 111.
23) Bandara, J., Mielczarski, J.A., Lopez, A. Kiwi, J., 2001. Sensitized degradation of chlorophenols on iron oxides induced by visible light comparison with titanium oxide, Applied Catalysis B: Environmental 34, 321- 333,
24) Sugiyama, S., Kastuma, K., Fukuda, N., Shono, T., Moriga, T. Hayashi, H., 2001. "Effect of the phase transition of iron (III) oxide on the oxidative dehydrogenation of propane in the presence and absence of tetrachloro methane, Catalysis Communications, 2(9), 285 – 290.
25) Grabowska, H., Klimkiewicz, R., Wrzyszcz, J., Syper, L., 2000. Catalytic reactions of pentamethylene and hexamethylene glycols over an iron oxide, Journal of Molecular Catalysis A: Chemical 154, 225 - 228.
26) Duma, V., Honicke, D., 2000. Gas phase epoxidation of propene by nitrous oxide over silica-supported iron oxide catalysts, Journal of Catalysis, 191**,** 93-104.
27) Dumaa, V., Poppa, K.E., Kung, M.C. Zhoub, H. Nguyenb, S., Ohyamac, S., Kung, H.H., Marshall, C.L., 2004. Gas phase oxidation of benzoic acid to phenol over nickel oxide catalysts, Chemical Engineering Journal 99, 227 - 236.
28) Wang, C.T., Willey, R.J., 1999. Fine particle iron oxide based aerogels for the partial oxidation of methanol, Catalysis Today, 52, 83 - 89.
29) Chou, S. Chihpin, H., 1999, Application of a supported iron oxyhydroxide catalyst in oxidation of benzoic acid by hydrogen peroxide, Chemosphere, 38, (12), 2719.
30) Wang, Y., Davis, B. H., 1999. Fischer-Tropsch synthesis, conversion of alcohols over iron oxide and iron carbide catalysts, Applied Catalysis A, 180**,** 277 -288.
31) Lauwiner, M., Roth, R., Rys, P., 1999. Reduction of aromatic nitro compounds with hydrazine hydrate in the presence of an iron oxide/hydroxide catalyst. III. The selective reduction of nitro groups in aromatic azo compounds, Applied Catalysis A, 177, 9 -14.
32) Benz, M., Vander Kraan, A.M. Prins, R., 1998. Reduction of aromatic nitrocompounds with hydrazine hydratein in the presence of an iron oxide hydroxide catalyst. Activity, X-ray diffraction and moessbauer study of the iron oxide hydroxide catalyst, "Applied Catalysis A: General 172, 149 - 155.
33) Baldrian, P., Vera, M., Gabriel, J., Nerud, F., Stopka, P., Martin H., Benes, M. J., 2006. Decolorization of synthetic dyes by hydrogen peroxide with heterogeneous catalysis by mixed iron oxides, Applied Catalysis B: Environmental, 66, 258 - 264.
34) Chaubal, N. S., Sawant, M. R., 2006. Synergistic role of aluminum in stabilization of mixed metal oxide catalyst for the nitration of aromatic compounds, Catalysis Communications, 7, 443 - 449.
35) Miller, S.L. and Orgel, L.E., 1974. The Origins of life on Earth, Prentice Hall, Inc., Englewood Clifts, N.J., P. 129-134, 83.
36) Paecht – Horowitz, M., Berger, J. and Katchalsky, A., 1970. Prebiotic synthesis of polypeptides by heterogeneous polycondensation of amino acid adenylates, Nature, 228, 636 – 639.
37) Wang, J., Zhu, Z.., Munir, A.., Zhou, H.S. 2011. Fe_3O_4 nanoparticles-enhanced SPR sensing for ultrasensitive sandwich bio-assay, Talanta, 84, 3, 783-788.
38) Chomoucka, J., Drbohlavova, J.,Huska, D., Adam, V., Kizek, R., Hubalek, 2010. Magnetic nanoparticles and targeted drug delivering, Pharmacological Research, , 62, 2, 144-149.
39) Kumar, C.S., Mohammad, F., 2011, Magnetic nanomaterials for hyperthermia-based therapy and controlled drug delivery, Advanced Drug Delivery Reviews, 63, 9, 789-808.