SURFACE CHARACTERISATION, ELECTRON DONATING ACID-BASE PROPERTIES AND CATALYTIC ACTIVITY OF Mg/Zn MIXED OXIDES

Final Report

Submitted to

The University Grants Commission

Principal Investigator

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Co-Investigator

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Preface

The acidic and basic properties of oxide catalysts are very important for the development of scientific criteria in catalyst application. The adsorption of molecules on to a surface is a necessary pre requisite to any surface mediated chemical process. Simple oxides only offer poor catalytic activity and selectivity when compared to multi component systems. Surface acidic and basic sites of catalysts are involved in the catalytic activity for various reactions such as cracking, isomerization, polymerization etc.

Over the past several years continuing interest is being shown on the application of advanced oxidation process for the treatment of hazardous pollutants in water. Of the various AOPs commonly employed in water treatment ultrasound irradiation has recently gained considerable attention as a means of catalyzing environmentally important reactions. Sono catalytic activity of metal oxides can be used to remove waste water pollutants.

No effort has so far been made to correlate the acid base properties, surface electron properties, catalytic and sono catalytic activity of Mg-Zn mixed oxide systems. This project gives emphasis on surface characterization, electron donating, acid base properties and catalytic activity of Mg-Zn mixed oxides of different composition.

Jalaja J.Malayan

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INTRODUCTION

INTRODUCTION

The adsorption of molecules on to a surface is a necessary prerequisite to any surface mediated chemical process. The elementary steps involved in a heterogeneously catalyzed reactions are in principle well known[1] .The surface electron properties of samaria,ceria and their mixed oxides with alumina have already been studied using electron acceptors like TCNQ and Chloranil[2,3] .Terephthalic acid adsorbed on to alumina surface from alcohol solution have been studied using inelastic tunneling microscopy[4]. The electron donor surface property of MgO is an intrinsic property of the surface[5]. Henderson et al showed that several oxides including MgO have the ability to decompose TNT[6]. In heterogenous catalysis dispersion increases the surface area available to the reactants . Sonocatalytic degradation of organic dyes have already been reported[7] .

According to Fuller[8] the correlation between catalytic activity and acid base properties of metal oxides can be explained by the strength and acid-base interactions between reacting molecules and catalyst surface. The generation of new acid sites on mixing two oxides was proposed by Thomas and coworkers[9]. The acid sites and base sites exist in adjacent positions on the surface of acid catalysts participating together in most of the reactions. Quantitative information on the base strength distribution of solid base surfaces were essential for the studies of solid base catalysis[10]. Binary metal oxides such as SiO_2-Al_2O_3, SiO_2-MgO, SiO_2-ZrO_2 and Al_2O_3 –B_2O_3 have been used as solid acid catalysts since their surface acidities are well known .

The surface properties of the heterogenous basic catalysts have been studied by various methods by which existence of the basic sites has been realized[11].The electron donating properties of Sm_2O_3 have been determined by the adsorption of electron acceptors of various electron affinity in solvents of different basicities. The extent of electron transfer from the oxide surface to the electron acceptor was determined from magnetic susceptibility measurements [2].Acid base properties of perovskite type mixed

oxides have been correlated with the catalytic activity of these oxides towards esterification of acetic acid using n-butanol[12] .Most of the acid base catalysts used in various chemical transformations are based on inorganic oxides. In most cases metal oxides are to be modified chemically or physically so as to get desired catalytic activity for a particular reaction. Most oxides because of their ability to take part in the exchange of electrons,protons or oxide ions are used as catalysts in both redox and base catalysis[13]. Electron donating and acid.base properties of cerium oxide and its mixed oxides with alumina was reported [14].

Ultrasonic irradiation of approximately 500kHz had been investigated for degradation of textile dye stuff [15]. According to Adevuyi so far four theories have been proposed to explain the sonochemical events , hot spot theory, electrical theory, plasma discharge theory and supercritical theory[16]. Malachite Green has now become a controversial compound due to the risks it poses to the consumers of the treated fish , including the effects on the immune system and reproductive system and its genotoxic and carcinogenic properties[17].Though the use of this dye has been banned in several countries and is now approved by US Food and Drug Administration, it is still being used in many part of the world due to the low cost, ready availability and efficacy[18].

A photo degradation of malachite green a cationic triphenyl methane dye is examined both under different p^H values and amounts of TiO_2[19]. Several recent investigations report successful removal of a wide range of organic pollutants from aqueous solutions in the range 20-1000kHz induces acoustic cavitation and it appears that the application of the novel means of reaction in the environmental remediation and pollution penetration is unlimited[16]. Of the various advanced oxidation processes commonly employed in the water treatment , ultrasound irradiation recently gained considerable attention as a means of catalyzing environmentally important reactions. Irradiation of aqueous solutions in the range 20-1000kHz induces acoustic cavitation which can be defined as the cyclic formation,growth and subsequent collapse of micro bubbles or cavities occurring in extremely small intervals of time and release large quantities of energy over a small location[20].

The degradation of methylene blue was used as a test reaction to verify the photo catalytic activity of the prepared TiO_2 nanoparticle suspensions[21]. Generally the adsorption of organic pollutants follow a Langmuir-Hinshelwood mechanism confirming the heterogenous catalytic character of the system with the reaction rate varying proportionally with the coverage[22,23].Over the past several years continuing interest is being shown on the application of advanced oxidation processes for the treatment of hazardous contaminants in water[24].

In this work we report the electron donating , acid-base properties and catalytic (sonocatalytic) activity of MgO-ZnO mixed oxides of different composition towards esterification and removal of organic pollutants like malachite green and methylene blue from their aqueous solutions. It has been observed that acid-base properties parallel the electron donating and catalytic activity of different MgO-ZnO mixed oxide systems.

EXPERIMENTAL

EXPERIMENTAL

Here we have studied the electron donating , acid-base properties and catalytic activity of MgO-ZnO mixed oxides of different composition (20% MgO-ZnO, 40% MgO-ZnO, 60%MgO-ZnO and 80%MgO-ZnO). Mixed oxides of different composition were prepared by co-precipitation method from their nitrate solutions. Samples of pure ZnO and MgO were prepared by hydroxide method.

The oxides were characterized using FTIR spectra and X-ray diffraction pattern Figs (1 – 8). The oxide surface generally terminated with surface hydroxyl groups which give strong IR bands in the region 4000-3000 cm^{-1}. The IR bands in 1600-1300 cm^{-1}(Finger print region) are assigned to O-H bending and metal oxide vibrations.

As all crystalline substance contribute to an overall powder X-ray diffraction patterns, the X-ray technique is routinely used to follow reaction and to monitor the purity of products. The reaction between MgO and ZnO to form $MgZnO_2$ may be monitored by powder X-ray diffraction. At the start of the reaction the mixture of MgO and ZnO will produce X-ray diffraction pattern containing those of pure phases. As the reaction proceeds a new set of reflections corresponding to the product $MgZnO_2$ emerges and grows in intensity at the expense of reflection from MgO and ZnO. On completion of reaction the powder diffraction pattern will be that of pure $MgZnO_2$. The 2θ peaks at 42.5^0 and 62.5^0 are specific to periclase (cubic) MgO, while other peaks are specific to Zincite (hexagonal) phase of ZnO.

d_{100}: d_{110}: d_{111} =   1:.719:1.254

1.688   1.215   2.103   (face centered cubic)

d_{110}:d_{002}:d_{101} = 2.76:2.58:2.45

This may be an indication that both MgO and ZnO are segregated but are physical mixtures. As the composition of ZnO increases the intensity due to ZnO peak increases. The surface area of different oxides were determined by BET method.

The surface area obtained are shown in Table I.

Table I

SAMPLE	SURFACE AREA (m^2/g)	PARTICLE SIZE (nm)
MgO	40.187	11
20% MgO-ZnO	19.889	17
40% MgO-ZnO	2.379	35
60% MgO-ZnO	3.9973	36
80% MgO-ZnO	4.1073	36
ZnO	4.0875	36

Average particle size has been estimated by using Debye-Scherrer formula.

$$D = .9\lambda / \beta cos\theta$$

where 'λ' is the wavelength of X-ray (541 nm). 'β' is FWHM (Full width at half maximum). 'θ' is the diffraction angle and 'D' is the particle diameter size. XRD confirms the crystal phase.

The BET analysis data.

Sample: MgO
Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-198.SMP

Started: 8/3/2013 9:02:49AM Analysis Adsorptive: N2

Completed: 8/3/2013 4:27:59PM Analysis Bath Temp.: -195.644 °C

Report Time: 8/3/2013 4:28:00PM Thermal Correction: No

Sample Mass: 0.3103 g Warm Free Space: 15.9646 cm³ Measured

Cold Free Space: 48.7586 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at 200° C 12 hrs

Surface Area

BET Surface Area: 40.1874 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 1053.687 Å radius at P/Po = 0.990745168: 0.181055 cm³/g

Sample: ZnO

Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-199.SMP

Started: 8/4/2013 8:44:40AM Analysis Adsorptive: N2

Completed: 8/4/2013 1:46:09PM Analysis Bath Temp.: -195.642 °C

Report Time: 8/4/2013 1:46:09PM Thermal Correction: No

Sample Mass: 0.7458 g Warm Free Space: 16.5582 cm³ Measured

Cold Free Space: 51.2643 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at 200° C 12 hrs

Surface Area

BET Surface Area: 4.0875 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 1654.173 Å radius at P/Po = 0.994137118: 0.012421 cm³/g

Sample: 80%MgO-ZnO

Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-200.SMP

Started: 8/4/2013 9:41:59PM Analysis Adsorptive: N2

Completed: 8/5/2013 3:50:40AM Analysis Bath Temp.: -195.628 °C

Report Time: 8/5/2013 3:50:40AM Thermal Correction: No

Sample Mass: 1.1530 g Warm Free Space: 14.8966 cm³ Measured

Cold Free Space: 45.1120 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at $200^{\circ}C$ 12 hrs

Surface Area

BET Surface Area: 4.1073 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 972.044 Å radius at P/Po = 0.989956424: 0.025065 cm³/g

Sample 60%MgO-ZnO

Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-201.SMP

Started: 8/5/2013 8:42:15AM Analysis Adsorptive: N2

Completed: 8/5/2013 2:30:31PM Analysis Bath Temp.: -195.629 °C

Report Time: 8/5/2013 2:30:31PM Thermal Correction: No

Sample Mass: 1.2452 g Warm Free Space: 15.8332 cm³ Measured

Cold Free Space: 48.1565 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at $200^{\circ}C$ 12 hrs

Surface Area

BET Surface Area: 3.9973 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 988.143 Å radius at P/Po = 0.990122391: 0.022094 cm³/g

Sample: 40% MgO-ZnO

Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-202.SMP

Started: 8/5/2013 3:50:51PM Analysis Adsorptive: N2

Completed: 8/5/2013 9:18:27PM Analysis Bath Temp.: -195.640 °C

Report Time: 8/5/2013 9:18:27PM Thermal Correction: No

Sample Mass: 0.9891 g Warm Free Space: 16.5967 cm³ Measured

Cold Free Space: 50.7634 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at $200^{o}C$ 12 hrs

Surface Area

BET Surface Area: 2.3793 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 1123.593 Å radius at P/Po = 0.991328523: 0.013158 cm³/g

Sample 20%MgO-ZnO

Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-203.SMP

Started: 8/6/2013 9:00:48AM Analysis Adsorptive: N2

Completed: 8/6/2013 6:44:23PM Analysis Bath Temp.: -195.595 °C

Report Time: 8/6/2013 6:44:23PM Thermal Correction: No

Sample Mass: 0.9357 g Warm Free Space: 15.1024 cm³ Measured

Cold Free Space: 44.7341 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at 200°C 12 hrs

Surface Area

BET Surface Area: 19.8890 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 607.280 Å radius at P/Po = 0.983799288: 0.128303 cm³/g

Sample: 10%MgO-ZnO

Operator: A Narayanan

Submitter: BASELIUS COLLEGE, KOTTAYAM

File: C:\2020\DATA\2013\EXT-204.SMP

Started: 8/6/2013 6:57:01PM Analysis Adsorptive: N2

Completed: 8/7/2013 7:01:56AM Analysis Bath Temp.: -195.621 °C

Report Time: 8/7/2013 7:01:55AM Thermal Correction: No

Sample Mass: 1.1778 g Warm Free Space: 15.8391 cm³ Measured

Cold Free Space: 48.0352 cm³ Equilibration Interval: 5 s

Low Pressure Dose: None Automatic Degas: Yes

Comments: Sample outgassed at 200°C 12 hrs

Surface Area

BET Surface Area: 24.1089 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 622.729 Å radius at P/Po = 0.984208497: 0.168683 cm³/g

XRD pattern are given in Figs 1-7.

Study of surface electron properties

The oxides were calcined in a muffle furnace at 300^0C for 2 hrs and activated at 500^0C for 2 hrs before each experiment. The surface electron properties of MgO, ZnO and their mixed oxides [20% MgO-ZnO, 50% MgO-ZnO and 80% MgO-ZnO] were determined using electron acceptors like TCNQ and Chloranil.

TCNQ – 7, 7, 8, 8 – Tetracyanoquinodimethane ($C_{12} H_4 N_4$)
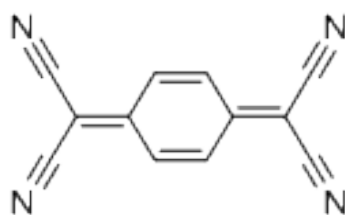
Electron affinity – 2.84 eV

Chloranil- 2, 3, 5, 6-Tetrachloro- 1, 4 –benzoquinnone ($C_6 Cl_4 O_2$)
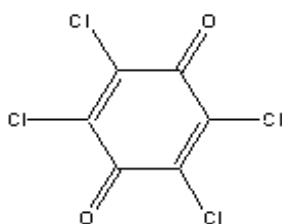
Electron affinity – 2.40 eV

The oxide (0.5 g), was then placed in a 250 ml conical flask and different concentrations of solutions of electron acceptors (TCNQ and Chloranil) in aceto nitrile was then added to the flask.
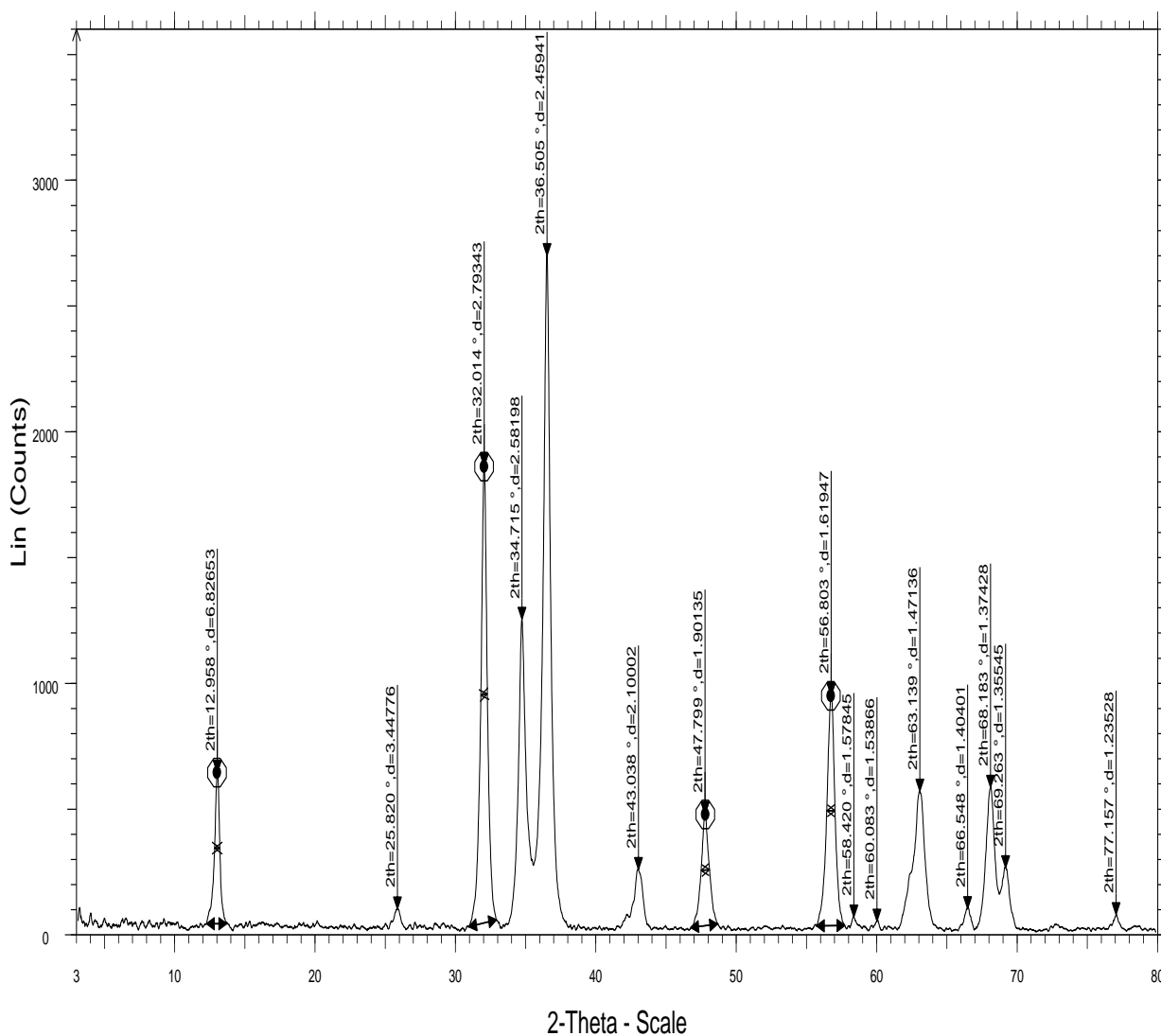
MgO

Sample IV - File: SAIFXR070224A-01(Sample IV).raw - Type: 2Th/Th locked - Start: 3.000 ° - End: 80.000 ° - Step: 0.010 ° - Step time: 0.2 s - Temp.: 25 °C (Room) - Time Star
1)   Sample IV - Left Angle: 41.170 ° - Right Angle: 44.510 ° - FWHM: 0.577 ° - Raw Area: 249.9 Cps x deg.
2)   Sample IV - Left Angle: 60.960 ° - Right Angle: 63.530 ° - FWHM: 0.042 ° - Raw Area: 126.9 Cps x deg.
Operations: Smooth 0.150 | Background 0.000,1.000 | Import

Fig 1 - MgO

SAMPLE-1

Fig 2- 20% MgO-ZnO

SAMPLE-2

Lin (Counts)

2th=7.028 ° ,d=12.56849
2th=9.684 ° ,d=9.12606
2th=12.804 ° d=6.90848
2th=31.947 ° ,d=2.79912
2th=33.357 ° ,d=2.68397
2th=34.603 ° d=2.59009
2th=36.419 ° ,d=2.46504
2th=47.706 ° ,d=1.90483
2th=56.744 ° ,d=1.62103
2th=63.010 ° ,d=1.47405
2th=66.484 ° ,d=1.40521
2th=68.084 ° d=1.37602
2th=69.212 ° ,d=1.35633
2th=72.689 ° ,d=1.29977
2th=77.073 ° ,d=1.23641

2-Theta - Scale

File: SAIFFXR130323E-02(SAMPLE-2).raw - Step: 0.020 ° - Step time: 31.2 s - WL1: 1.5406 - kA2 Ratio: 0.5 - Generator kV: 40 kV - Generator mA: 35 mA - Type: 2Th/Th lock
1) Obs. Max: 31.945 ° - FWHM: 0.358 ° - Raw Area: 47.15 Cps x deg. - Net Area: 45.36 Cps x deg.
2) Obs. Max: 34.603 ° - FWHM: 0.363 ° - Raw Area: 33.50 Cps x deg. - Net Area: 30.90 Cps x deg.
3) Obs. Max: 36.424 ° - FWHM: 0.378 ° - Raw Area: 81.59 Cps x deg. - Net Area: 77.41 Cps x deg.
4) Obs. Max: 47.702 ° - FWHM: 0.426 ° - Raw Area: 16.75 Cps x deg. - Net Area: 15.49 Cps x deg.
5) Obs. Max: 56.740 ° - FWHM: 0.445 ° - Raw Area: 27.22 Cps x deg. - Net Area: 25.29 Cps x deg.
6) Obs. Max: 63.009 ° - FWHM: 0.485 ° - Raw Area: 23.21 Cps x deg. - Net Area: 21.99 Cps x deg.
Operations: Smooth 0.176 | Background 3.162,0.000 | Import

Fig 3- 40% MgO-ZnO

SAMPLE-5
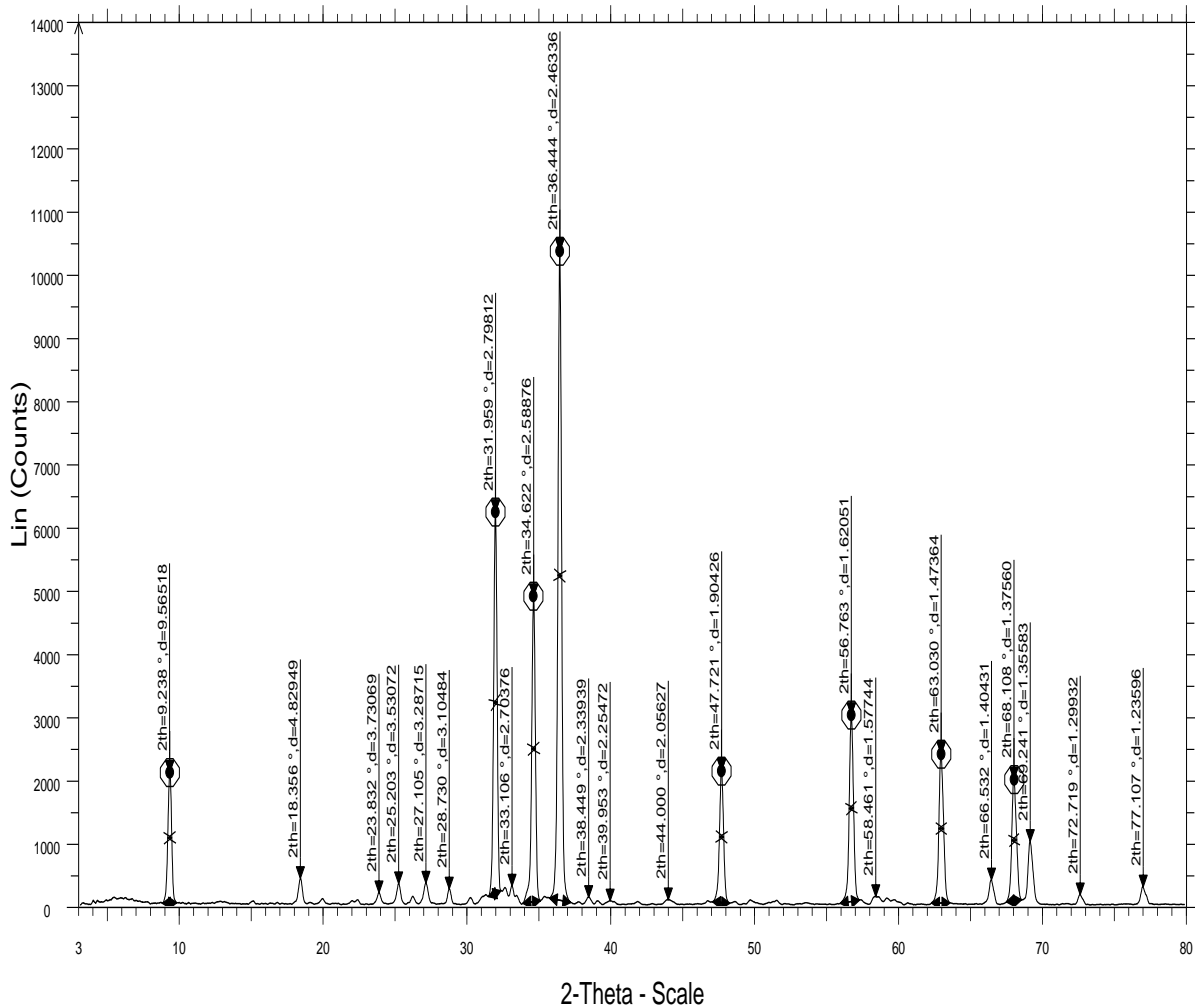
File: SAIFFXR130323E-05(SAMPLE-5).raw - Step: 0.020 ° - Step time: 31.2 s - WL1:

1) Obs. Max: 9.249 ° - FWHM: 0.285 ° - Raw Area: 21.66 Cps x deg. - Net Area: 20.
2) Obs. Max: 31.951 ° - FWHM: 0.264 ° - Raw Area: 59.72 Cps x deg. - Net Area: 5
3) Obs. Max: 34.612 ° - FWHM: 0.274 ° - Raw Area: 49.58 Cps x deg. - Net Area: 4
4) Obs. Max: 36.437 ° - FWHM: 0.273 ° - Raw Area: 104.1 Cps x deg. - Net Area: 1
5) Obs. Max: 47.717 ° - FWHM: 0.305 ° - Raw Area: 24.31 Cps x deg. - Net Area: 2
6) Obs. Max: 56.763 ° - FWHM: 0.314 ° - Raw Area: 35.44 Cps x deg. - Net Area: 3
7) Obs. Max: 63.022 ° - FWHM: 0.348 ° - Raw Area: 30.20 Cps x deg. - Net Area: 2

8) Obs. Max: 68.101 ° - FWHM: 0.356 ° - Raw Area: 25.81 Cps x deg. - Net Area: 2
   Operations: Smooth 0.150 | Background 0.457,0.000 | Import
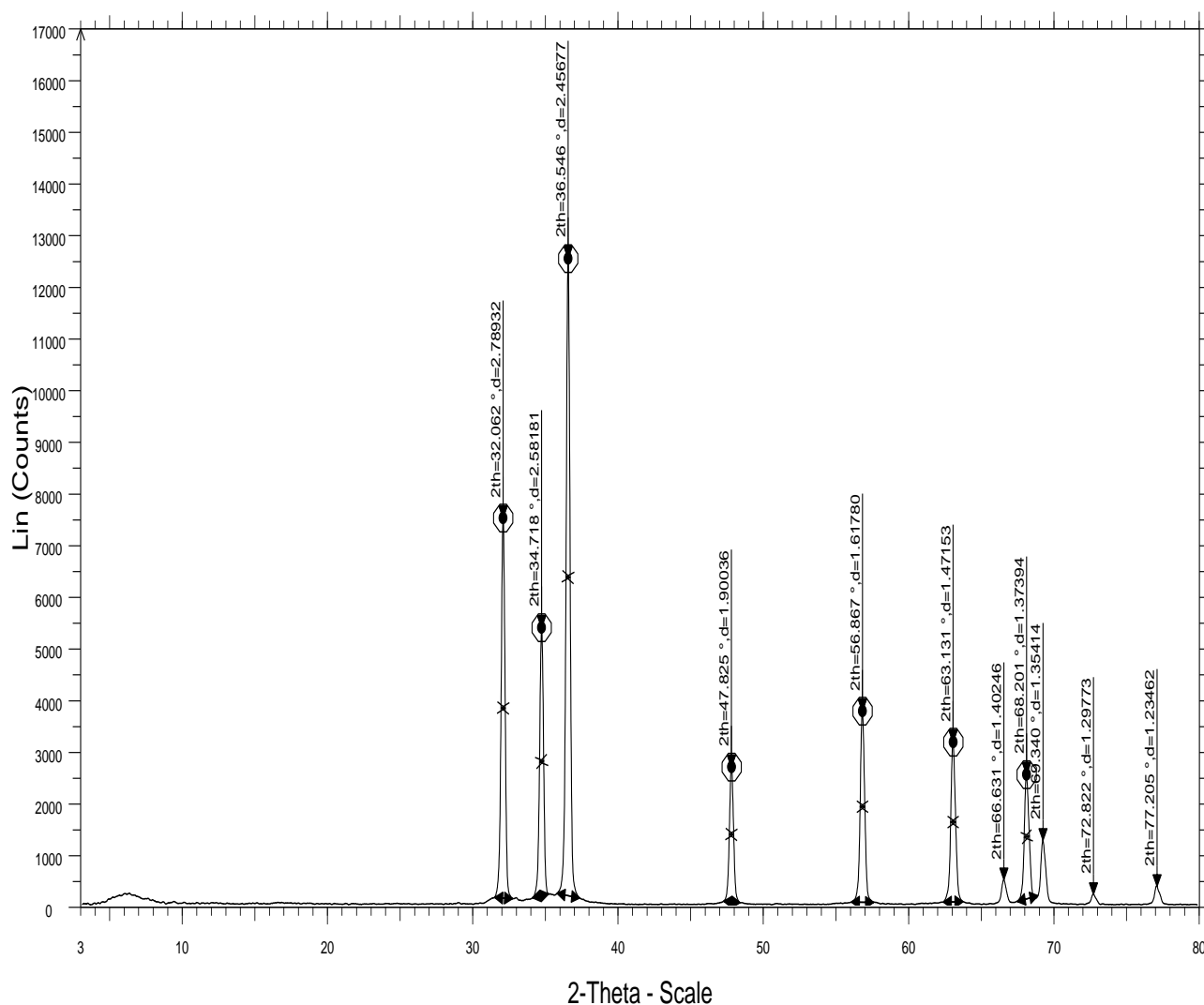
Fig 4- 50% MgO-ZnO
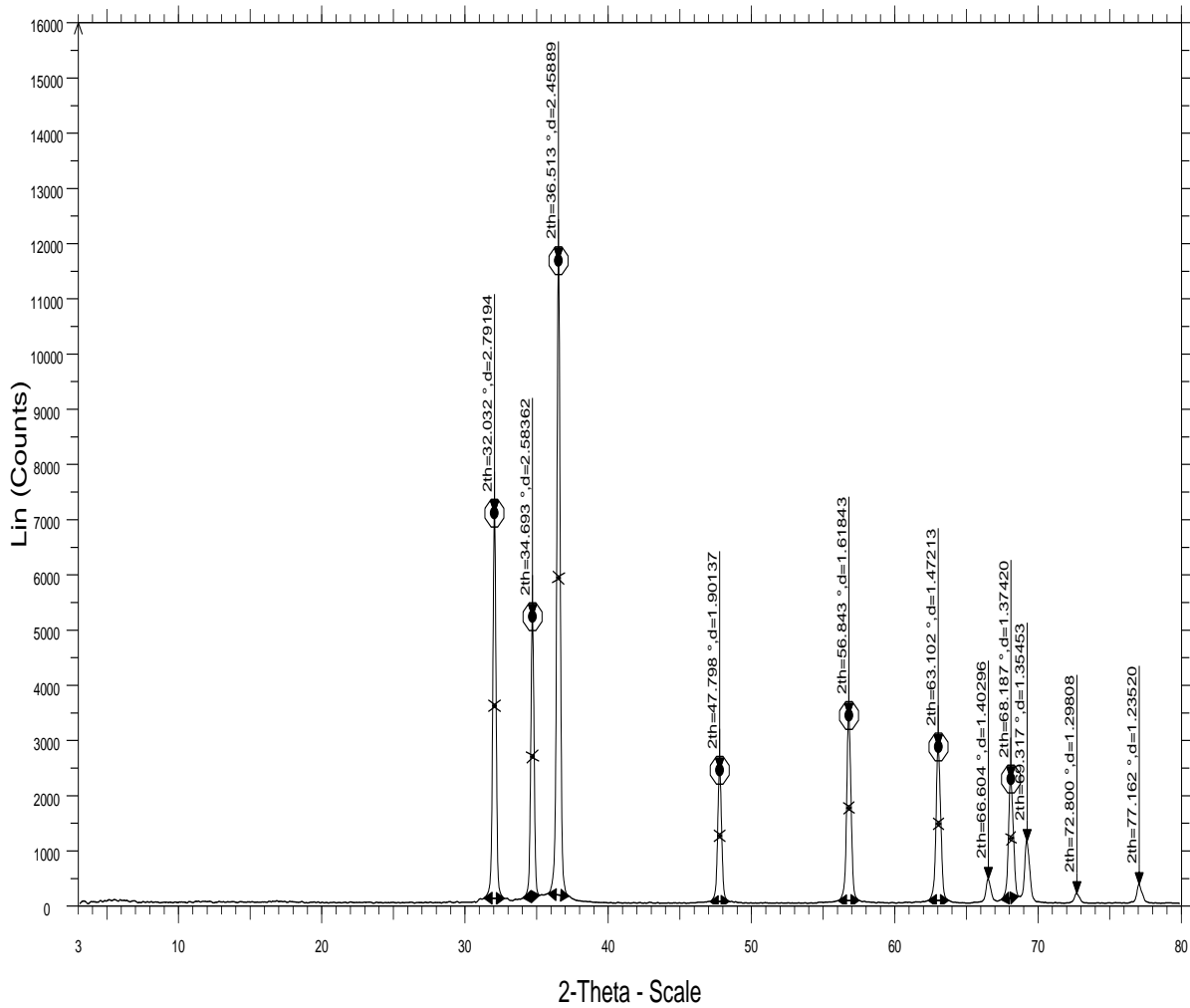
SAMPLE-4

File: SAIFFXR130323E-04(SAMPLE-4).raw - Step: 0.020 ° - Step time: 31.2 s - WL1:   Operations: Smooth 0.150 | Background 0.031,0.000 | Import

1) Obs. Max: 32.027 ° - FWHM: 0.251 ° - Raw Area: 67.20 Cps x deg. - Net Area: 6
2) Obs. Max: 34.688 ° - FWHM: 0.253 ° - Raw Area: 49.92 Cps x deg. - Net Area: 4
3) Obs. Max: 36.511 ° - FWHM: 0.262 ° - Raw Area: 115.8 Cps x deg. - Net Area: 1
4) Obs. Max: 47.794 ° - FWHM: 0.301 ° - Raw Area: 27.46 Cps x deg. - Net Area: 2
5) Obs. Max: 56.833 ° - FWHM: 0.328 ° - Raw Area: 42.16 Cps x deg. - Net Area: 3
6) Obs. Max: 63.098 ° - FWHM: 0.354 ° - Raw Area: 37.64 Cps x deg. - Net Area: 3
7) Obs. Max: 68.173 ° - FWHM: 0.371 ° - Raw Area: 31.82 Cps x deg. - Net Area: 2

Fig 5- 60% MgO-ZnO

22

SAMPLE-3

Lin (Counts)

2th=32.062 °,d=2.78932
2th=34.718 °,d=2.58181
2th=36.546 °,d=2.45677
2th=47.825 °,d=1.90036
2th=56.867 °,d=1.61780
2th=63.131 °,d=1.47153
2th=66.631 °,d=1.40246
2th=68.201 °,d=1.37394
2th=69.340 °,d=1.35414
2th=72.822 °,d=1.29773
2th=77.205 °,d=1.23462

2-Theta - Scale

File: SAIFFXR130323E-03(SAMPLE-3).raw - Step: 0.020 ° - Step time: 31.2 s - WL1:   Operations: Smooth 0.150 | Background 0.031,0.000 | Import
1) Obs. Max: 32.062 ° - FWHM: 0.292 ° - Raw Area: 81.04 Cps x deg. - Net Area: 7
2) Obs. Max: 34.720 ° - FWHM: 0.293 ° - Raw Area: 59.35 Cps x deg. - Net Area: 5
3) Obs. Max: 36.548 ° - FWHM: 0.295 ° - Raw Area: 138.7 Cps x deg. - Net Area: 1
4) Obs. Max: 47.828 ° - FWHM: 0.308 ° - Raw Area: 30.57 Cps x deg. - Net Area: 2
5) Obs. Max: 56.865 ° - FWHM: 0.332 ° - Raw Area: 46.38 Cps x deg. - Net Area: 4
6) Obs. Max: 63.123 ° - FWHM: 0.350 ° - Raw Area: 41.05 Cps x deg. - Net Area: 3
7) Obs. Max: 68.196 ° - FWHM: 0.357 ° - Raw Area: 35.18 Cps x deg. - Net Area: 2

Fig 6- 80% MgO-ZnO

SAMPLE-6

Fig 7-ZnO
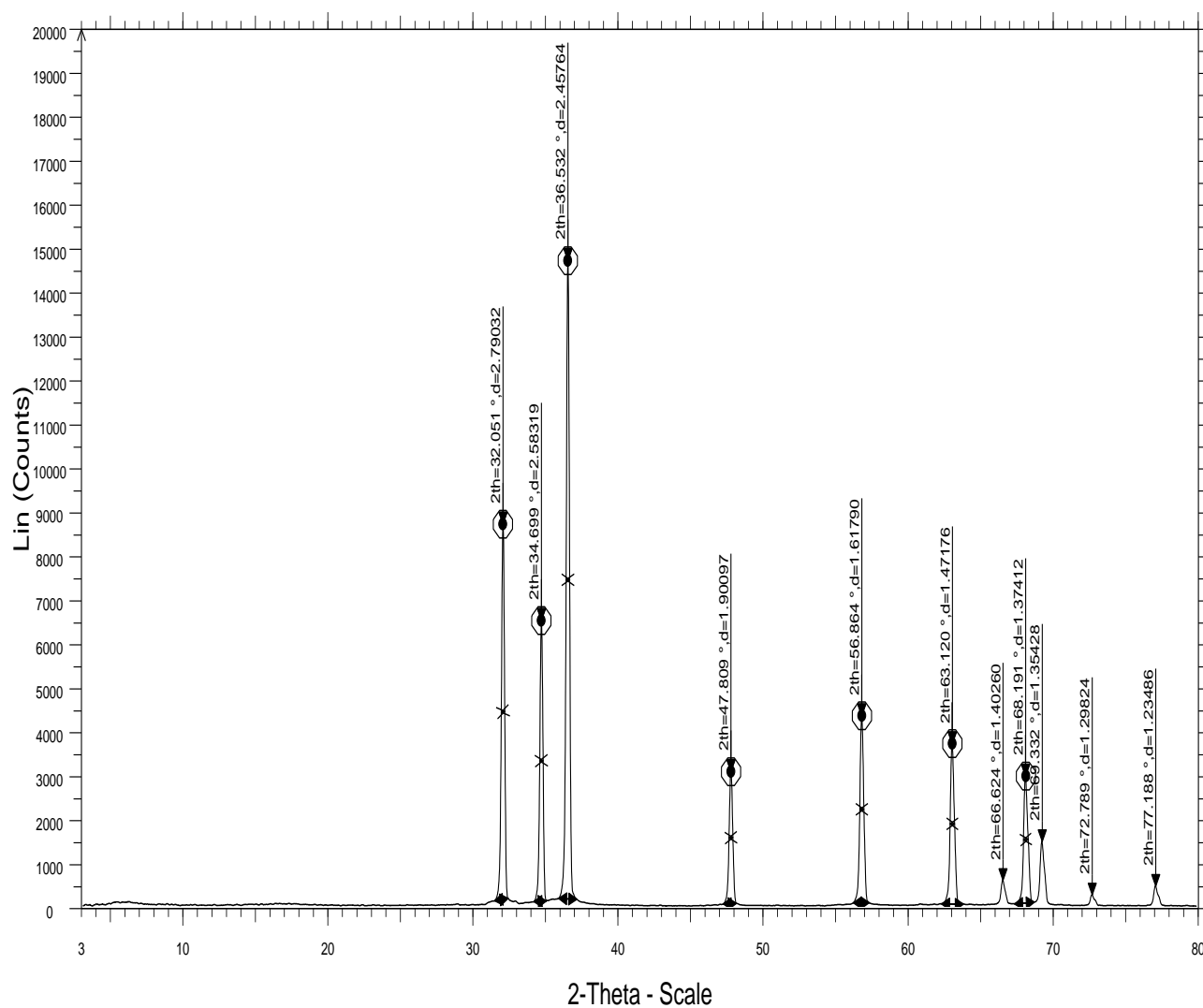
File: SAIFFXR130323E-06(SAMPLE-6).raw - Step: 0.020 ° - Step time: 31.2 s - WL1:   Operations: Smooth 0.150 | Background 0.000,0.000 | Import

1) Obs. Max: 32.048 ° - FWHM: 0.241 ° - Raw Area: 76.05 Cps x deg. - Net Area: 7
2) Obs. Max: 34.703 ° - FWHM: 0.237 ° - Raw Area: 55.83 Cps x deg. - Net Area: 5
3) Obs. Max: 36.533 ° - FWHM: 0.248 ° - Raw Area: 133.7 Cps x deg. - Net Area: 1
4) Obs. Max: 47.809 ° - FWHM: 0.271 ° - Raw Area: 30.23 Cps x deg. - Net Area: 2
5) Obs. Max: 56.851 ° - FWHM: 0.290 ° - Raw Area: 46.40 Cps x deg. - Net Area: 4
6) Obs. Max: 63.103 ° - FWHM: 0.311 ° - Raw Area: 42.83 Cps x deg. - Net Area: 4
7) Obs. Max: 68.176 ° - FWHM: 0.327 ° - Raw Area: 36.10 Cps x deg. - Net Area: 3
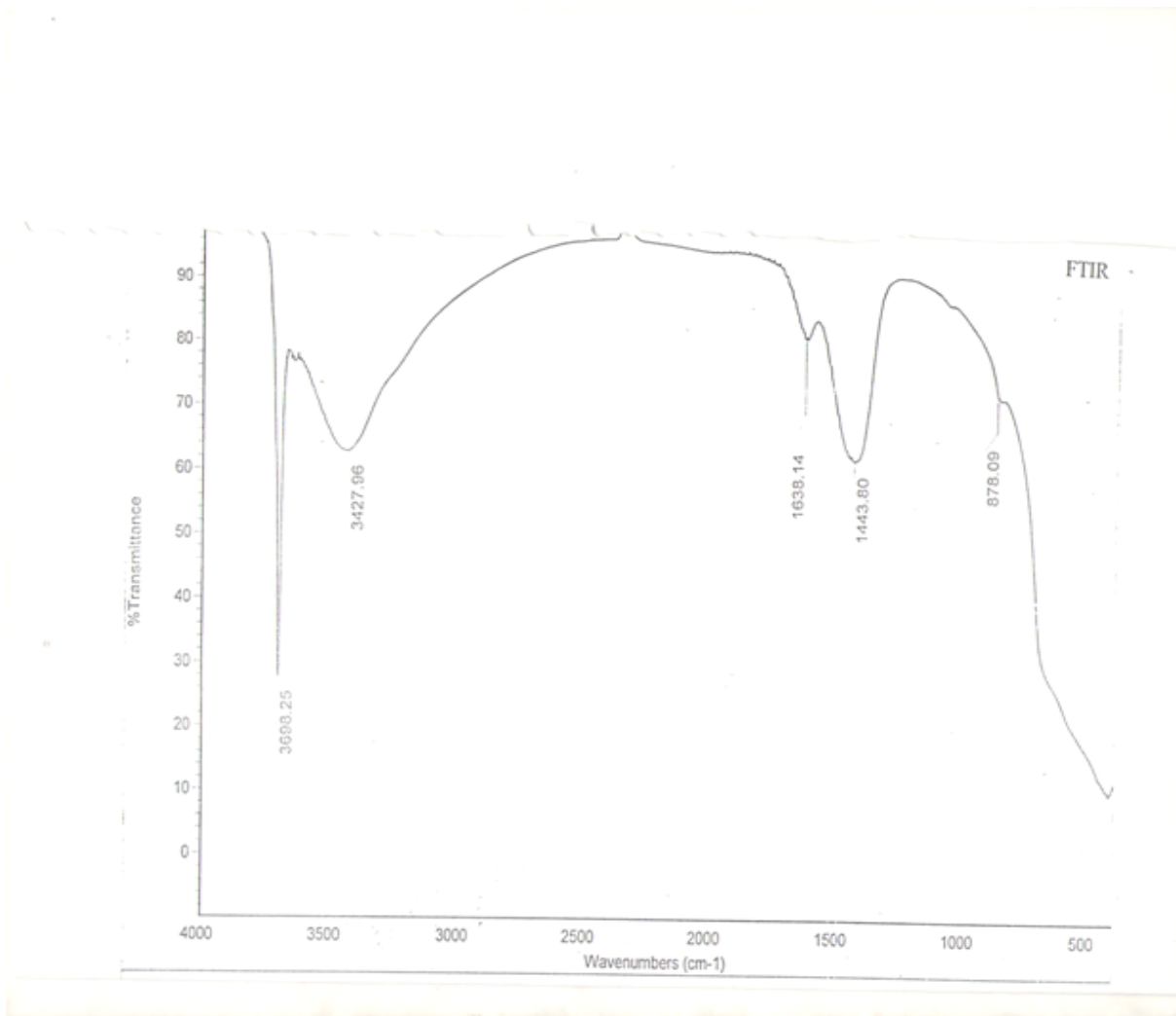
Fig 8 -   IR Spectra of MgO

After the solution had subsequently been stirred for 1hr in a thermo stated shaker at 25^0C, the solution was centrifuged and centrifugate was taken for spectrophotometric analysis. Calculations are based on the Beer Lambertz's law.

$A = \varepsilon bc$

A – Absorbance

ε – Molar absorptivity (molecular mass ×absorptivity)

b – The path length in cm
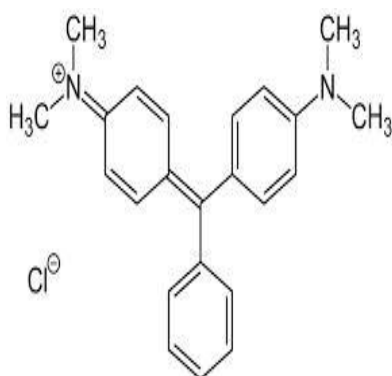
c – Concentration in moles/litre

The amount of electron acceptor adsorbed was determined from the difference in concentration of the solution before and after adsorption. The absorbance of electron acceptor was measured by means of UV visible spectro photometer at the λ_{max} of the electron acceptor in the solvent. 393.5nm For TCNQ in acetonitrile and 288nm for Chloranil in acetonitrile. When TCNQ was adsorbed on the catalyst surface the corresponding TCNQ anion radicals were formed on the catalyst surface. The samples coloured by the adsorption of electron acceptor gave unresolved esr spectra with g value of 2.003 corresponding to TCNQ radicals. Chloranil gave no adsorption.

Study of catalytic activity

The esterification reaction was carried out in a 50 ml round bottomed flask equipped with a reflux condenser in which the catalyst(0.5g) ,acetic acid (2m mol) and n-butanol (32m mol) and n-decane was used as the internal standard .The reaction temperature was maintained at 98^0C and stirred using magnetic stirrer for 5 hours .The reaction was also carried out using a sonicator(Ultrasonic frequency-42MHz).The product was analyzed by means of GCMS and TLC. The GCMS data are shown .

The catalytic activity of these oxides of nano dimension was studied for environmentally important reactions i.e; sonocatalytic degradation of dyes like Malachite green and Methylene blue. The reaction was followed by absorbance measurement using UV-visible spectrophotometry Figs(9-16). The reaction was carried out using a sonicator, ultrasound frequency (42MHz). An aqueous dispersion of oxide was prepared by adding 50mg of activated oxide powder in a 100ml solution containing the respective dye (100ppm). Prior to sonication the mixture was repeatedly stirred for 30min to ensure the establishment of adsorption/desorption equilibrium. The structure of malachite green and methylene blue are as follows-

bis (p-dimethylamino phenyl)phenyl methyliumchloride

$C_{23}H_{25}ClN_2$
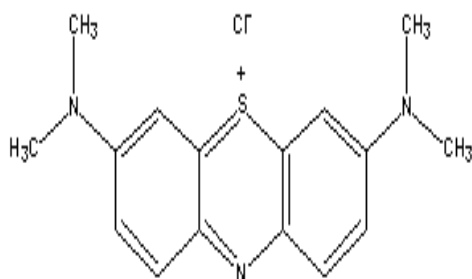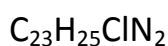
3,7-bis (Dimethylamino)phenothiazin-5-ium-chloride

$C_{16}H_{18}N_3SCl$
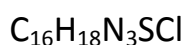
<u>GCMS</u>

1. GCMS – 60% MgO-ZnO stirrer

2. GCMS – 60% MgO-ZnO sonicator

3. GCMS – 80% MgO-ZnO stirrer

4. GCMS – 80% MgO-ZnO sonicator

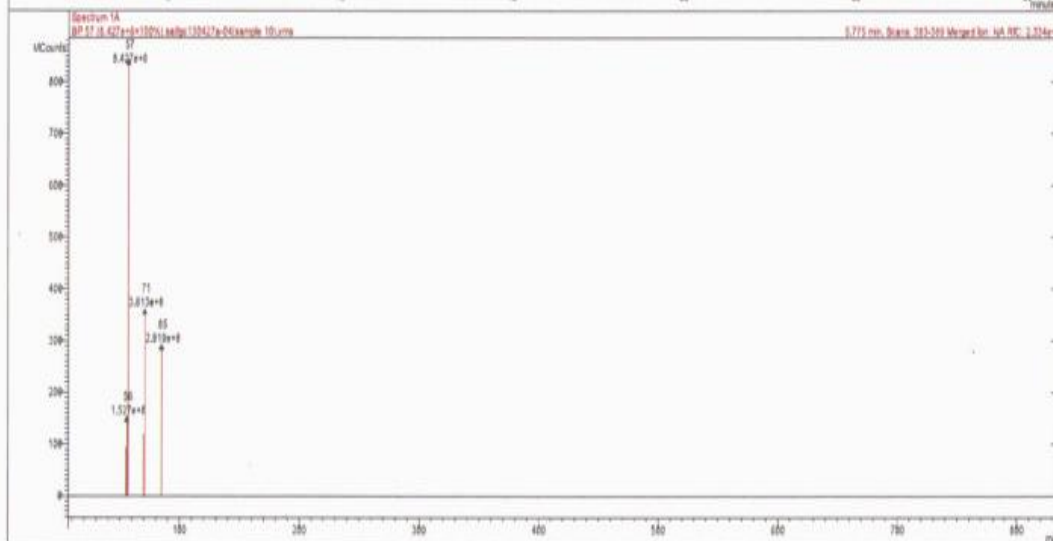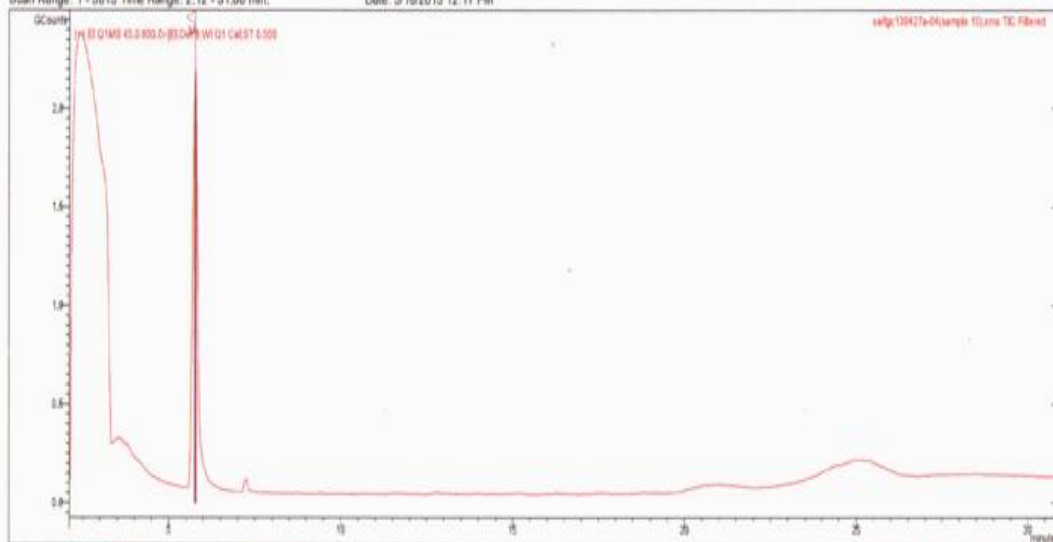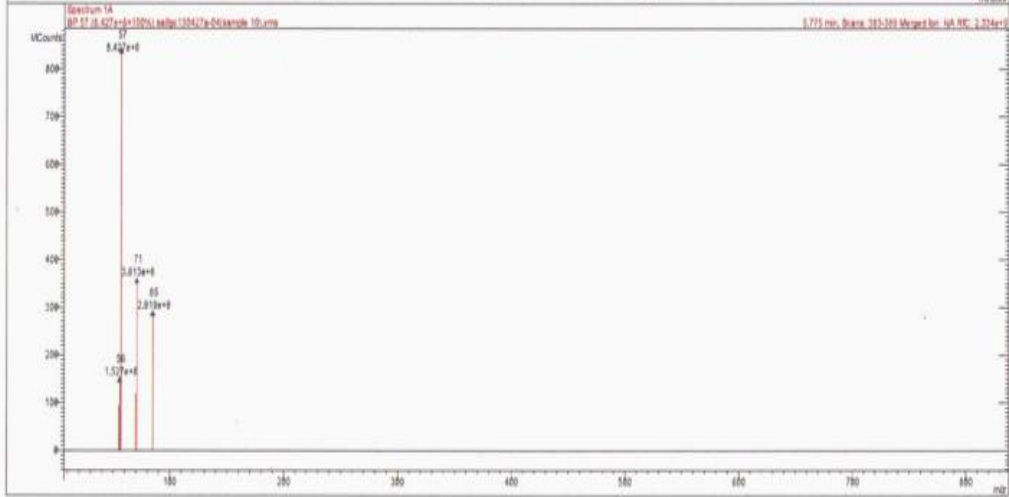5. GCMS –ZnO stirrer

6. GCMS -ZnO sonicator

GCMS

GCMS – ZnO using stirrer

MS Data Review Active Chromatogram and Spectrum Plots - 5/16/2013 3:45 PM

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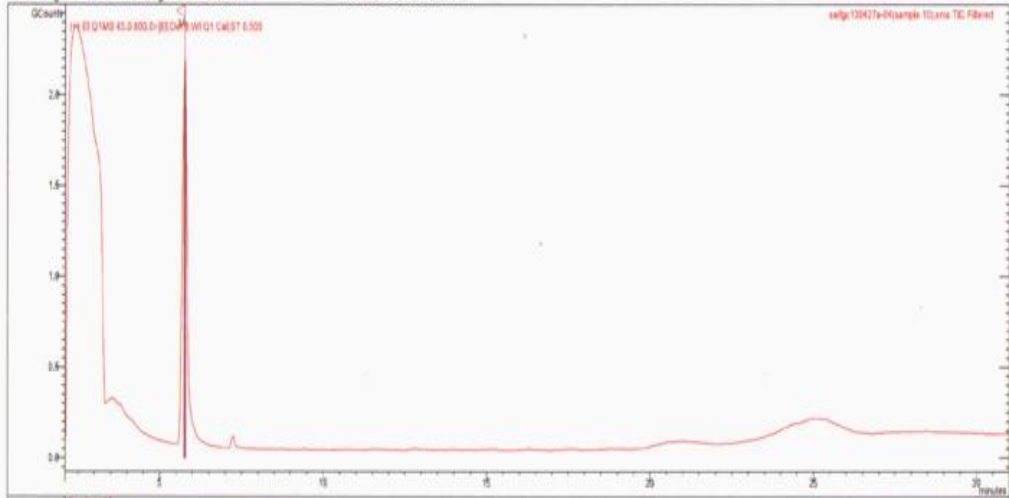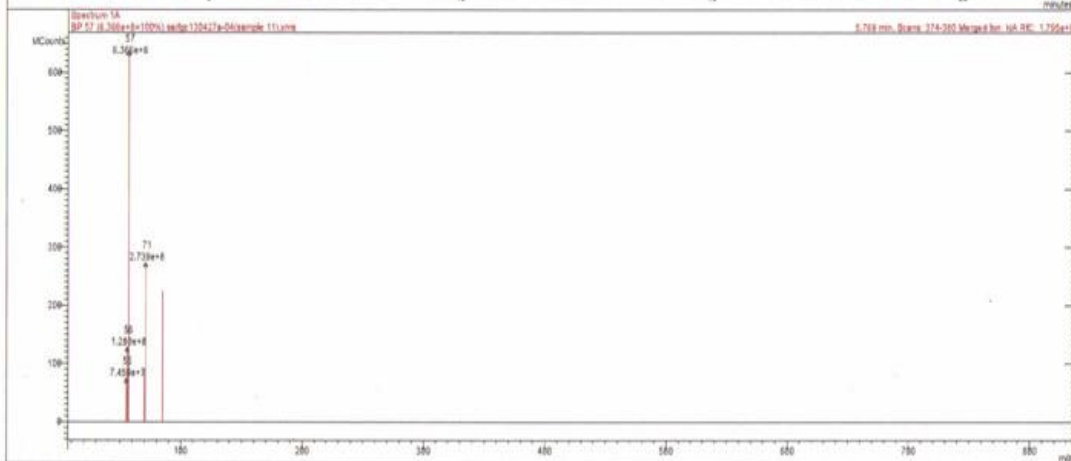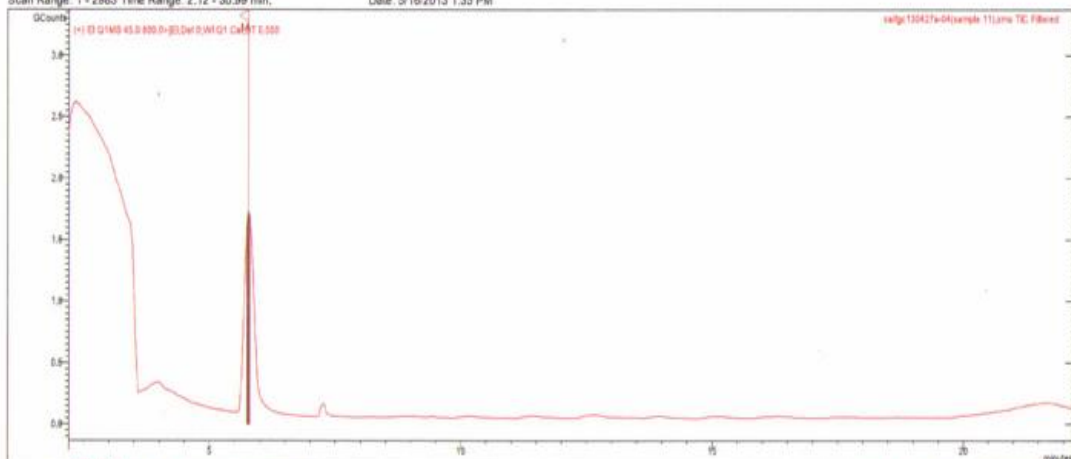

GCMS – ZnO using sonicator

PDF created with FinePrint pdfFactory Pro trial version http://www.pdffactory.com

GCMS – 80% MgO-ZnO stirrer

MS Data Review Active Chromatogram and Spectrum Plots - 5/16/2013 3:51 PM

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80% MgO-ZnO sonicator

32

MS Data Review Active Chromatogram and Spectrum Plots - 5/16/2013 3:39 PM

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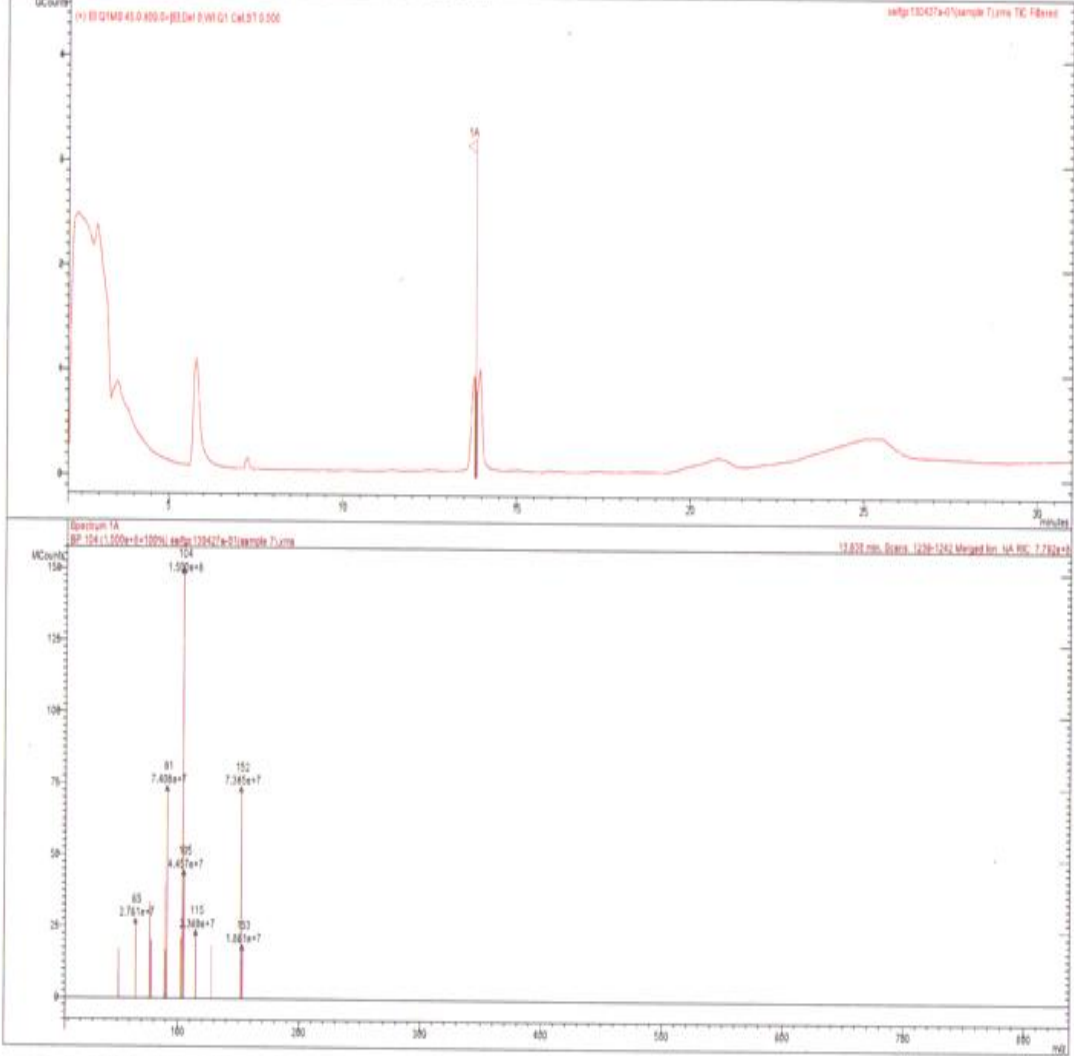Scan Range: 1 - 3037 Time Range: 2.12 - 31.00 min.   Date: 5/15/2013 2:53 PM

GCMS -60%MgO-ZnO stirrer

MS Data Review Active Chromatogram and Spectrum Plots - 5/16/2013 3:41 PM

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60% MgO-ZnO Sonicator

Fig 9   MgO amd 20% MgO-ZnO+MG

MG – Malachite Green

Figure 10:   40% MgO -ZnO after adsorption of MG

Figure 11:   40% MgO -ZnO before adsorption of MG

Figure 12:   60% MgO -ZnO after adsorption of MG

Figure 13: 60% MgO -ZnO before adsorption of MG

Figure 14:   80%MgO - ZnO before adsorption of MG
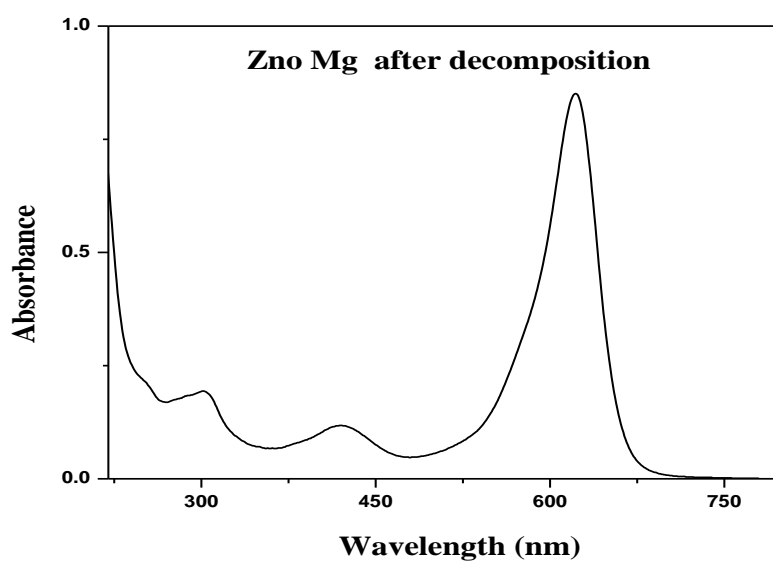
Figure 15: 80% MgO - ZnO after adsorption of MG
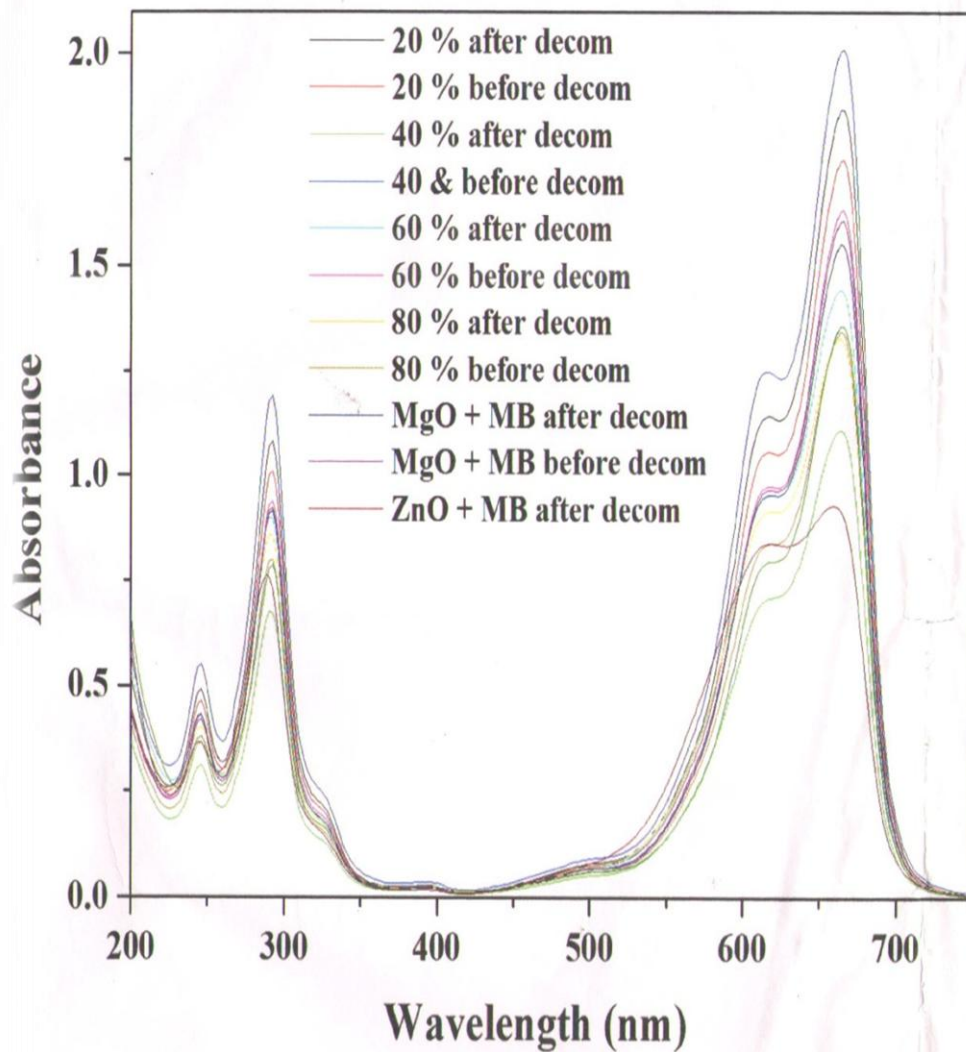
Fig 16: Mg-Zn Mixed Oxides+Methylene Blue

Studies on acid ity-basicity of mixed oxide systems

The oxides were sieved to prepare powders of 100-200 mesh size, and then activated at a particular temperature (500^0c) for 2 hours prior to each experiment.
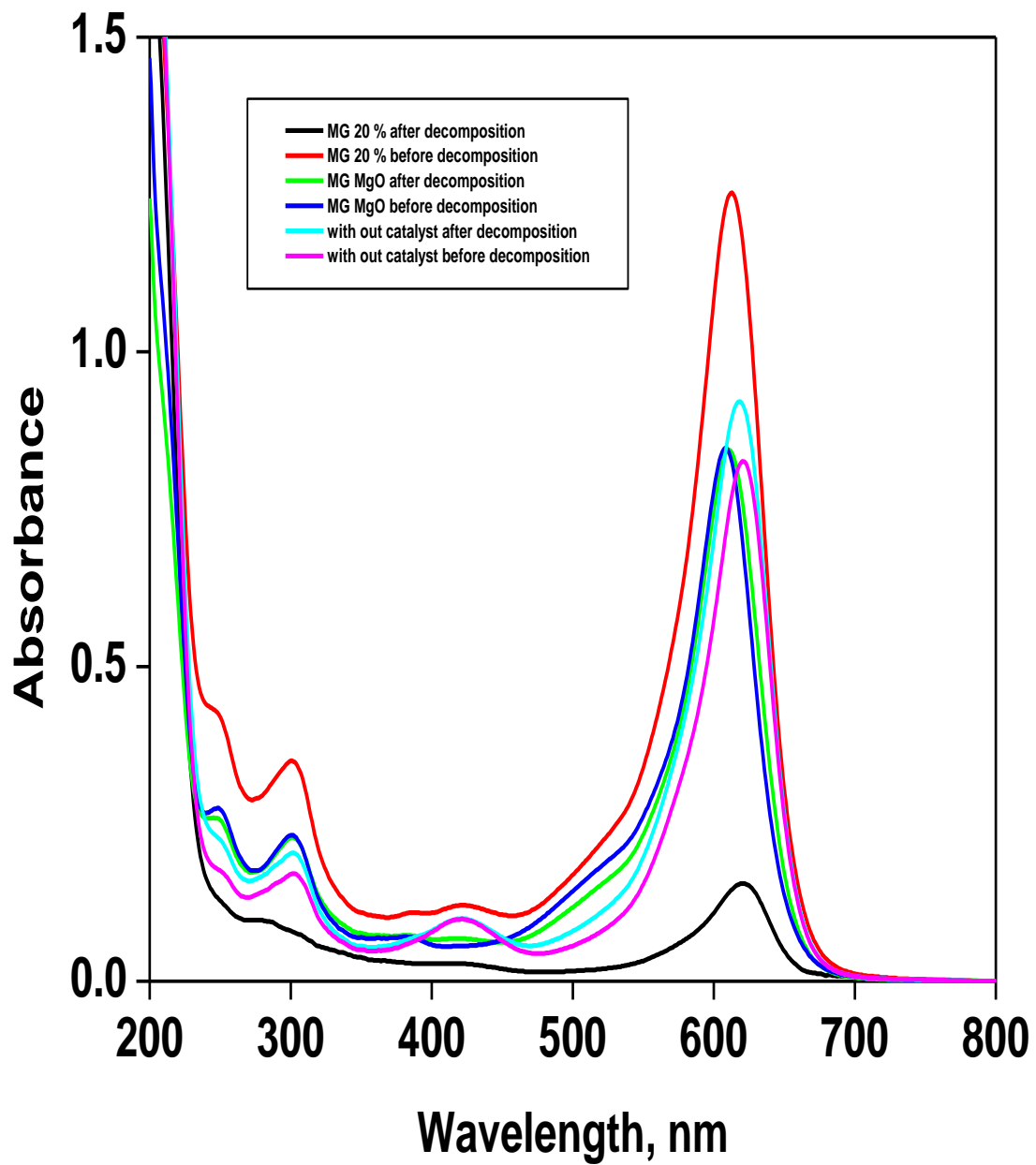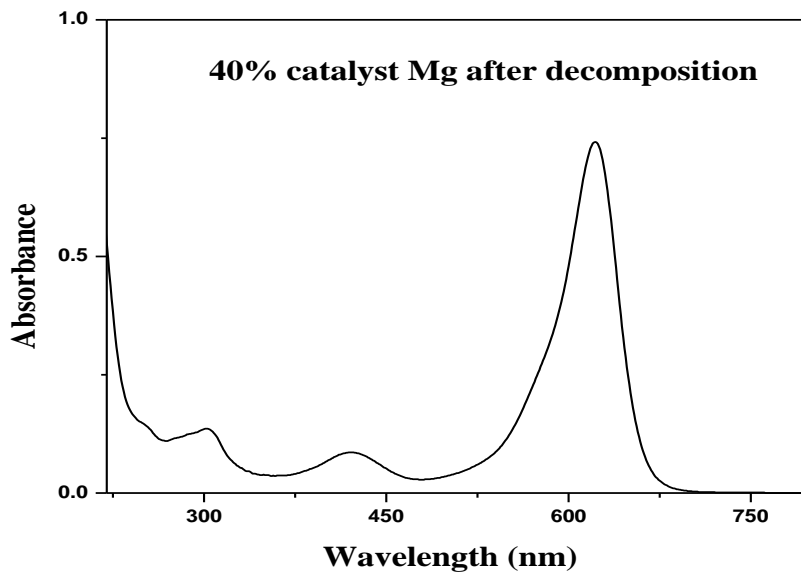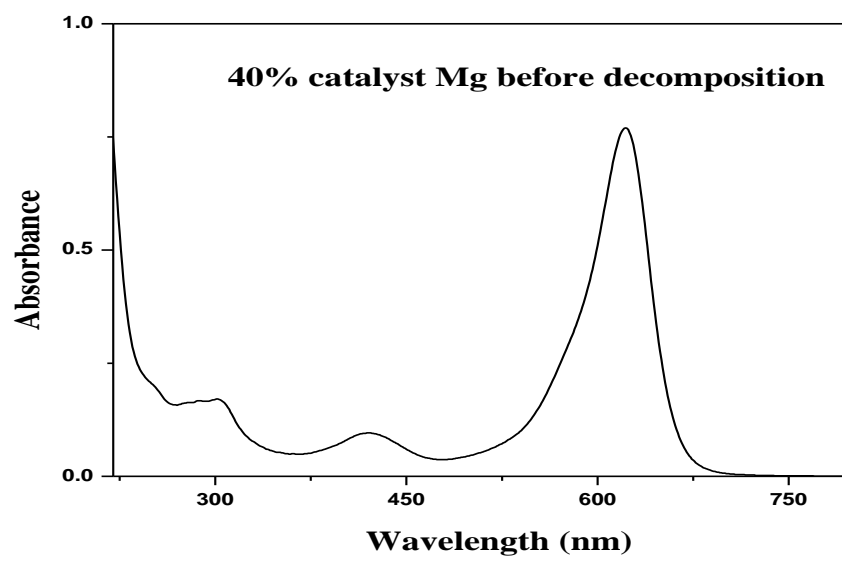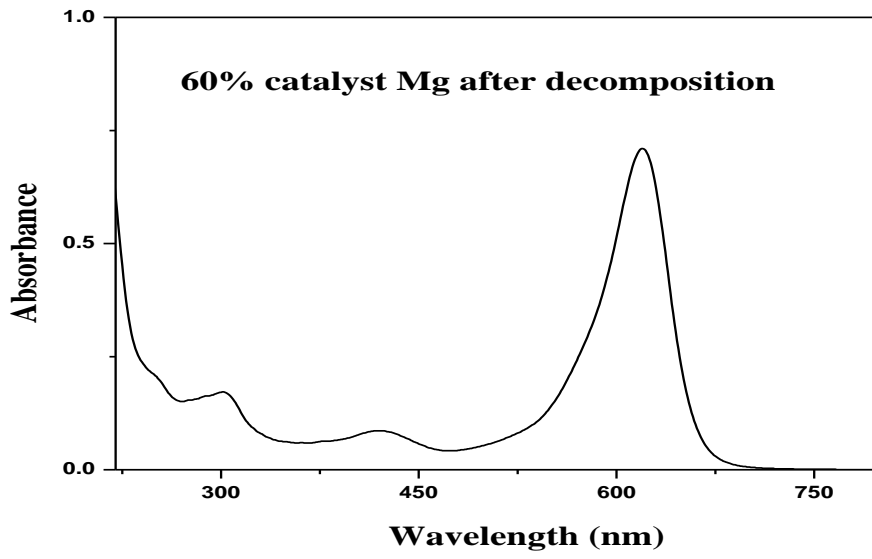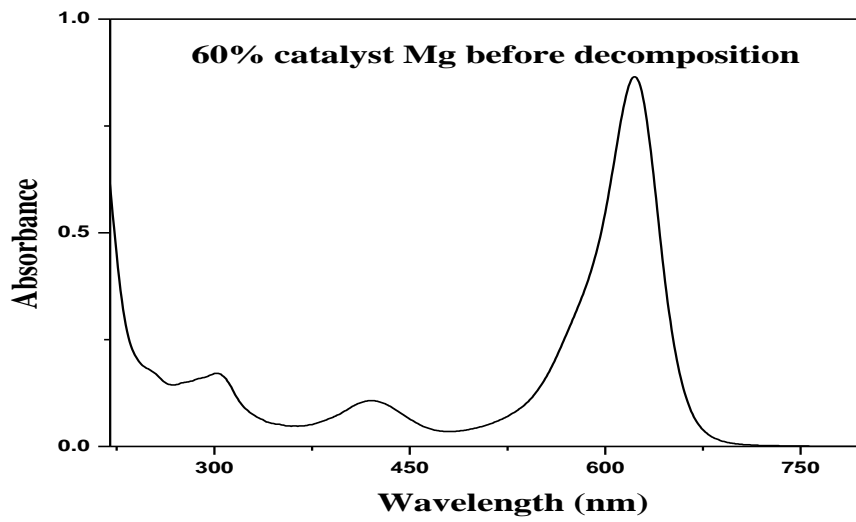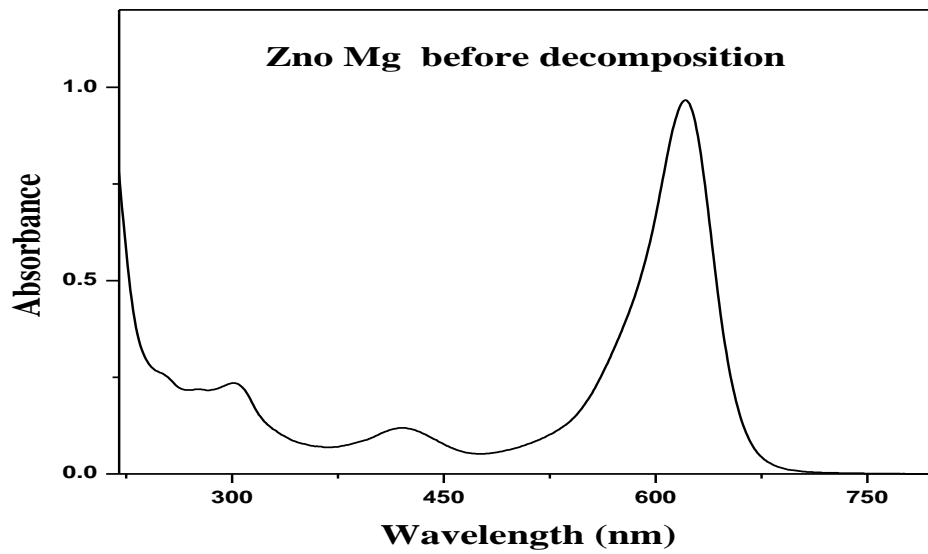
The acidity at various acid strength of solid was measured by titrating 0.1g of solid suspended in 5ml benzene with a 0.1N solution of N-butyl amine in benzene at the endpoint basic colour of the indicator appeared.

The basicity was measured by titrating 0.1g of solid suspended in 5ml benzene with a 0.1N solution of trichloro acetic acid in benzene using the same indicator as those for acidity measurement . The colour of the indicator on the surface at the endpoint of the titration were the same as the colours which appeared by adsorption of respective indicators, on the acid sites . As the result for the titration lasting 1 hour was the same as those for a titration lasting 20 hours, 1 hour was taken for titration.

Benzene used for acidity and basicity measurements was purified by the following procedures. Benzene obtained from Qualigens was shaken repeatedly with about 15% of the volume of conc.H_2SO_4 in a stoppered separating funnel unless the acid layer is colourless on standing. After shaking the mixture is allowed to settle and lower layer was drawn off it was then washed twice with water to remove most of the acid, then with 10% sodium carbonate solution and finally with water. It was dried with anhydrous $CaCl_2$. It was then boiled and fraction boiling at 80^0c was collected.

HAMMETT INDICATORS USED FOR STUDY

- ➢ METHYL RED
- ➢ DIMETHYL YELLOW
- ➢ NEUTRAL RED
- ➢ BROMO THYMOL BLUE

The acidic and basic colours are as shown below in TABLE II .

TABLE II

Hammett indicators	pk_a	colour	
		basic	acidic
Dimethyl yellow	+3.3	Yellow	Red
Methyl red	+4.8	Yellow	Red
Neutral red	+6.8	Yellow	Red
Bromo thymol blue	+7.2	Blue	Yellow

Trichloro acetic acid (SQ Grade obtained from Qualigens Fine Chemicals) and N-butyl amine (S.d fine chemicals pvt.Ltd.) were used without further purification.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Though Mg-Zn mixed oxides are widely used as catalysts in various types of industries and are well known for photo catalytic activity no effort has so far been made to understand the surface properties of these oxides. The adsorption isotherms are classified as Langmuir type. The adsorption isotherms were drawn by plotting the amount of electron acceptor adsorbed (mol/g) against the equilibrium concentration (mol/dm^3) Figs (16 -20). Of the two electron acceptors chloranil shows no adsorption. When TCNQ was adsorbed the surface of the oxide showed remarkable coloration, i.e., bluish green for TCNQ. This is due to the interaction between electron acceptor adsorbed on the surface with the oxide. From the Langmuir plots the limiting amount of electron acceptor adsorbed was determined The data are shown in Table: III.

It was reported that surface hydroxyl ions and electrons trapped in intrinsic defects (in band gap region) are responsible for electron transfer. The amount adsorbed on ZnO is lowest due to its strong Lewis acidity. Pure MgO exhibit the highest relative concentration of high strength basic sites. Lewis acidity is due to exposed metal ions. The acidic character of the metal surface depends on the electro negativity of the metal in the periodic table. The greater the covalency of the oxide, the higher the value of the charge/radius ratio, the more likely acidity in to be found. But an oxide with a low value of ratio is more ionic in nature and will present more basic sites.

Here the acidic character or the decrease in electron donating properties are found to be in an order MgO<20% MgO-ZnO <50%MgO-ZnO <80%MgO-ZnO < ZnO. Thus strength of an electron donor site can be expressed in terms of the electron affinity of the electron acceptor which can form anion radicals on the adsorption site. Hence the limit of electron transfer of oxide surface is between 2.88 and 2.40 eV in acetonitrile which is a weak base solvent. This indicates that the oxide surface acts as electron donor to electron acceptors with electron affinity

greater than 2.84 eV but not to those with electron affinity lower than 2.40 eV. Incorporation of ZnO introduces moderate acidity neutralizing the strong basic sites of MgO.

The amount of electron acceptor adsorbed depends on the activation temperature of the oxide, basicity of the solvent, the electron affinity of the electron acceptor and electron donor properties of the oxide catalyst.

TABLE III

SAMPLE	LIMITING AMOUNT ADSORBED ($\times 10^{-3}$ mol/g)
Pure MgO	8.9790
20%MgO/ZnO	1.8130
50%MgO/ZnO	1.0260
80%MgO/ZnO	0.4986
Pure ZnO	0.3672

The sonocatalytic activity of the oxide systems was tested towards esterification and decomposition of dyes like malachite green and methylene blue. . In the esterification the product formed according to the following reaction

$$CH_3COOH + C_4H_9OH \longrightarrow CH_3COOC_4H_9 + H_2O$$
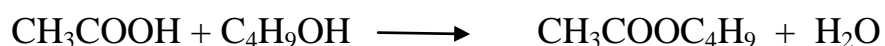
The results obtained from GCMS are shown in Table IV ,
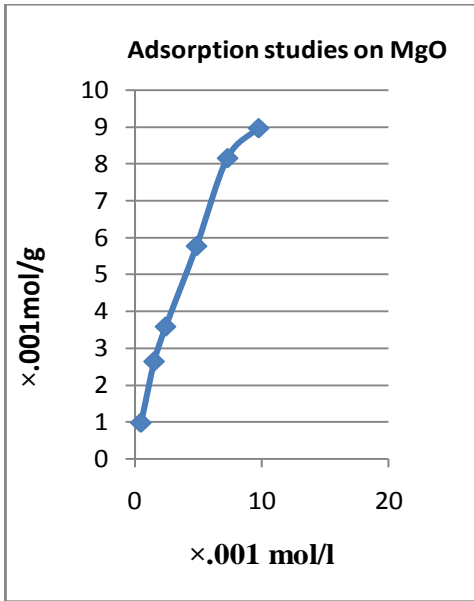
Fig.16
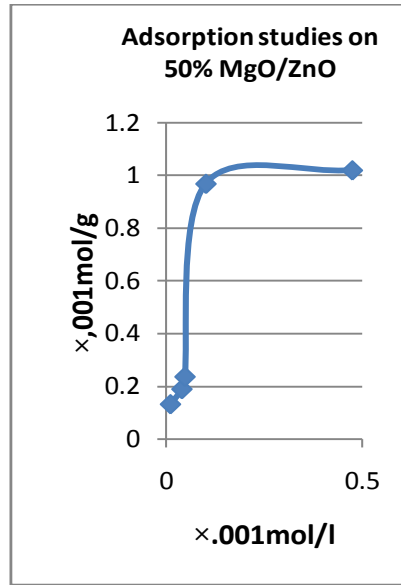
Fig.17
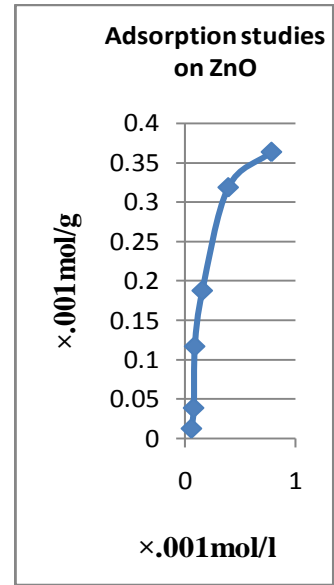
Fig 18
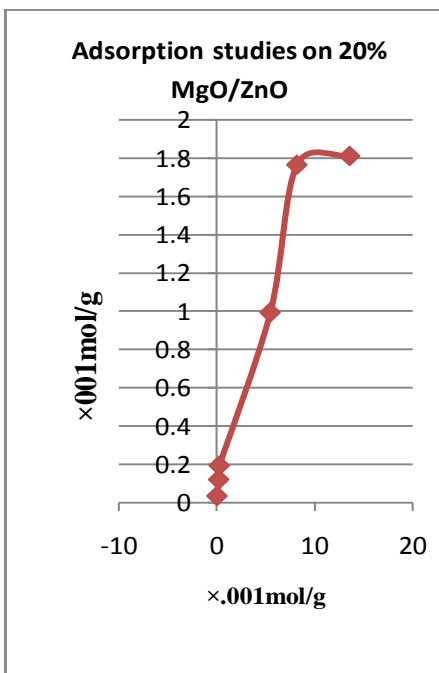
Fig19
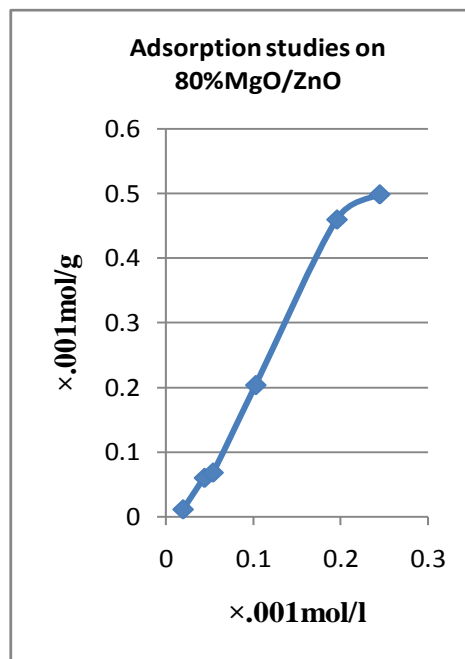
Fig 20

Table IV

Sample		% conversion (from mass count)
60% MgO-ZnO	1.Stirrer	15
	2.Sonicator	29
80% MgO-ZnO	1.Stirrer	64
	2.Sonicator	37
ZnO	1.Stirrer	83
	2.Sonicator	62
MgO	1.Stirrer	No conversion
	2.Sonicator	No conversion

Of the oxides 10%,20%,50%,60%,80%,ZnO and MgO , 10% MgO-ZnO,20%,50% and MgO gave negative response to TLC .Above samples were given for GCMS analysis .The H^+ ions on the surface layer of catalyst can catalyze the reaction In the mass spectrum the X-axis represent the M/Z ratios. The Y-axis represents the signal intensity for each of the fragments detected during the scan .

The ionizing of n-butyl acetate can be represented as

$$CH_3-\underset{\underset{O}{\|}}{C}-O-C_4H_9 \longrightarrow CH_3CO^+$$
$$m/e =43$$

$$C_4H_9COO^+ \longrightarrow m/e =101$$

$$C_4H_9O^+ \longrightarrow m/e =63$$

$$C_4H_9^+ \longrightarrow m/e =57$$

$$CH_3COO\ CH^+CH_3 \longrightarrow m/e =87$$
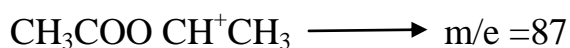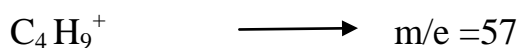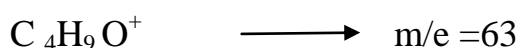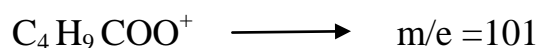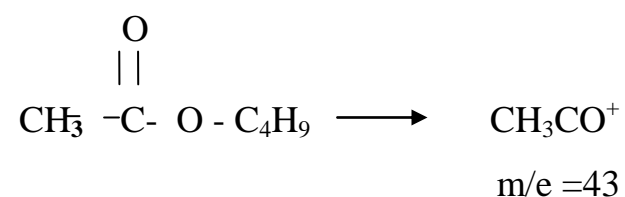
m/e 43 is the base peak for ester and n- decane(internal standard) , m/e 56 is the base peak for n-butanol. Here % conversion can be found out from the signal intensity. α-cleavage at carbonyl group yields the large m/z at 43 ion ,m/e = 101 can be produced by an additional α-cleavage reaction induced by the saturated oxygen atom , a similar cleavage with lose of the largest group producers the significant 87 m/e peak. $C_4H_9^+$ gives m/e peak at 57.The size of the spectral peak is proportional to the amount of substance that reaches the detector on the GC instrument. The amount of time that a compound is retained on the GC column is known as the retention time .The retention time for n-butyl acetate is found to be around 3min .

A probable mechanism for the esterificaion process is proposed considering the generation of H^+ , RO^+ and RCOOH on the photo catalyst surface . The heterogeneous sono catalytic process is by the use of ultra sound in chemical reactions in solution provides specific activation based on a physical phenomenon acoustic cavitation. Cavitation is a process in which mechanical activation destroys the attractive forces of molecules in the liquid phase .Applying ultrasound compression of the liquid is followed by expansion in which a sudden pressure drop forms small oscillating bubbles of gaseous substances. These bubbles expand with each cycle of the applied ultrasonic energy until they reach an unstable size they can then collide and violently collapse .Besides bringing about mechanical effects cavitation induced by sonication can promote many homogeneous and heterogeneous reaction by generating radicals which give rise to chain reaction in solution.

ZnO is an acidic oxide and MgO is a basic oxide. It was found that MgO-ZnO mixed oxides and pure oxides contain both Bronsted OH groups and Lewis acid sites provided by metal cations. Incorporation of ZnO in the lattice of MgO introduces moderate acidity neutralising the strong basic sites of MgO. Because of the presence of isolated O^{2-} basic centres pure MgO exhibited poor and low activity. The catalytic activity of the oxide surface towards esterification decreases in the following order ZnO > 80% MgO/ZnO > 60% MgO/ZnO > MgO in the case of both stirrer and

sonicator methods .It has also been reported that MgO and ZnO are good photo catalysts.

Here we have also studied the son catalytic activity of MgO-ZnO mixed oxides of different composition towards the decomposition of malachite green and methylene blue. Malachite Green is a heterocyclic aromatic chemical compound $C_{23}H_{25}N_2Cl$. The solution is green in colour.Molecular weight is 365 and λmax is equal to 617nm. Methylene Blue is a basic cationic dye. It is a hetero cyclic aromatic compound with molecular formula $C_{16}H_{18}N_3SCl$ and molecular weight 319.85 and λmax is equal to 663nm. The main sources of waste water generated by the textile industry originate from the washing and bleaching of natural fibres and from the dyeing and finishing steps. The waste water cannot be adequately treated in conventional waste water treatment plant.

Here we have done the sonocatalytic degradation of malachite green (MG) and methylene blue (MB) which have absorption maximum at 617nm and 664nm respectively using 20% MgO-ZnO, 40% MgO-ZnO, 60% MgO-ZnO, 80% MgO-ZnO pure oxides and without catalyst.   The absorbance of the system was measured using a UV-Visible spectrophotometer.The values obtained for the two systems are shown below. No decomposition was observed for systems without catalyst, i.e, only under pure   sonication. For 20% mixed oxide system strongly adsorbed Malachite green undergoes a slight decomposition as shown by broadness of the absorbtion peak. The colour of the solution after sonication also changed to light green indicated that the decomposition of Malachite green may occur and N-demethlyated intermediate may be formed. (P-dimethylamino phenyl) (P-methylaminophenyl) phenyl methylium has absorption maximum at 608nm. The sonication was carried out for 2hrs.

Table V MG decomposition (1ppm solution)

CATALYST	BEFORE ADSORBTION	AFTER ADSORTION
20% MgO- ZnO	1.228	0.153
40% MgO- ZnO	1.050	0.850
60% MgO- ZnO	.910	0.766
80% MgO- ZnO	1.060	1.060
MgO	0.766	0.807
ZnO	0.46	0.46
Without catalyst	0.813	0.920

Table-VI MB decomposition

CATALYST	BEFORE ADSORBTION	AFTER ADSORTION
20% MgO-ZnO	2.0106	1.1023
40% MgO-ZnO	1.6311	1.4371
60% MgO-ZnO	1.8689	1.7484
80% MgO-ZnO	1.6061	1.5498
MgO	1.3577	.9087
ZnO	1.3406	1.3203

No peak shift (no degradation) was observed for 40% and 60% mixed oxide system. The surface area of 20% mixed oxide system in higher compared to other oxide systems. On MgO surface the cationic dye cannot be properly get adsorbed. The oxide surface would be negatively charged in aqueous solution due to the presence of surface hydroxyl group. Both dyes get adsorbed on the catalyst surface. The basicity of the mixed oxide system increases in the following order ,   MgO> 20%

MgO-ZnO> 40% MgO-ZnO > 60% MgO-ZnO> 80% MgO-ZnO> ZnO as determined by Hammett-Indicator method. The results are shown in Table VII. The acid-base strength distribution curves ,Figs (21-27) meet at a point on the abscissa, H_{0MAX} where acidity=basicity = 0. H_0, max can be regarded as a structural parameter to represent the acid-base properties of solids which is sensitive to the surface structure. It is known that a solid with a large –ve H_0, max value has weak basic sites and a solid with a large +ve H_0max value has strong basic sites.

Table VII

Mixed oxides	Surface area	Basicity meq/m^2			Acidity meq/m^2			H_0 max
		$H_0\geq3.8$	$H_0\geq4.8$	$H_0\geq7.2$	$H_0\leq3.3$	$H_0\leq4.8$	$H_0\leq7.2$	
MgO	40.187	0.271	0.134		---	---	0.180	6.2
20% MgO-ZnO	19.889	0.560	0.346		---	---	0.126	5.9
40% MgO-ZnO	2.3793	4.40	2.60		---	---	5.10	5.75
60% MgO-ZnO	3.9973	3.30	1.40		---	---	1.15	5.6
80% MgO-ZnO	4.1073	2.14	1.14		---	---	2.58	5.5
ZnO	4.0675	2.07	1.08		---	---	2.83	5.45

MgO is highly basic and fineness of the particles are also higher. The surface of basic oxides is negatively charged and cationic dyes get adsorbed on the surface. The *ad*sorption of the substrate on to catalyst surface directly affects the occurrence of
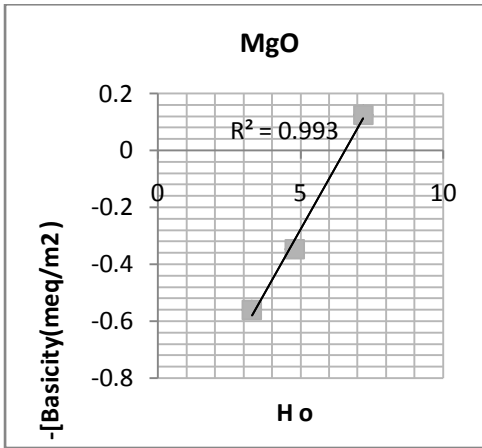
H0,max =6.60
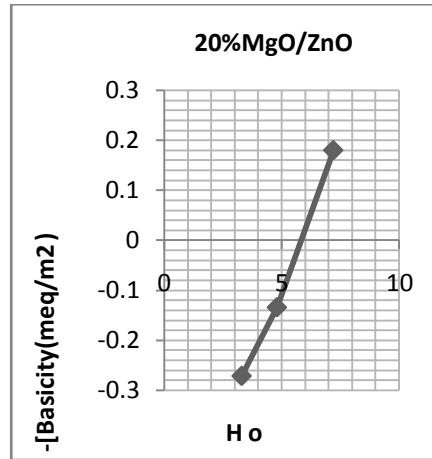
Ho,max = 5.82

Ho,max = 5.62

Ho,max =5.47

Ho,max =5.43

Ho,max =5.40

Figs 21-27 acid-base strength distribution curves

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electron transfer between the cationic dye and oxide system. For MG high adsorption occurs on 20% mixed oxide system and slight adsorption occurs for 40% and 60% mixed oxide system. As the acidity of the oxide surface increases the adsorption of the cationic dye particles is decreased.

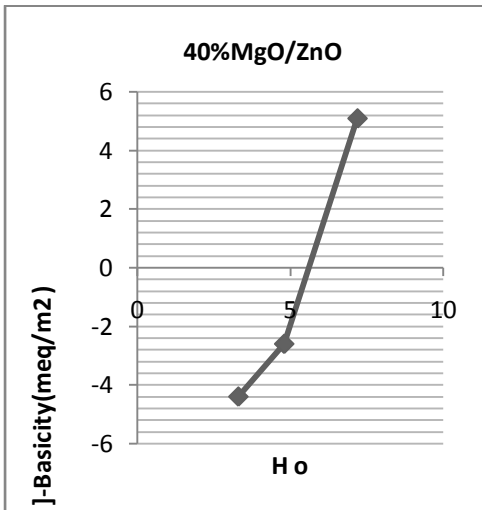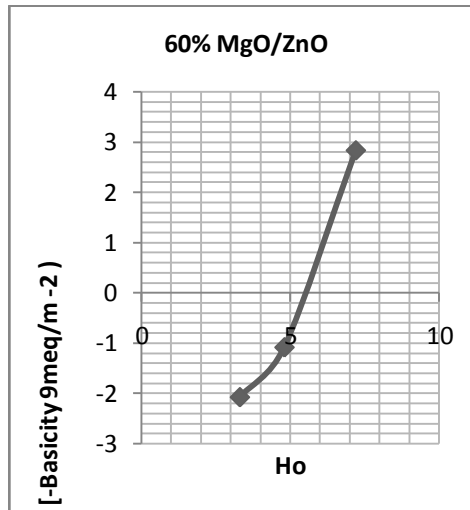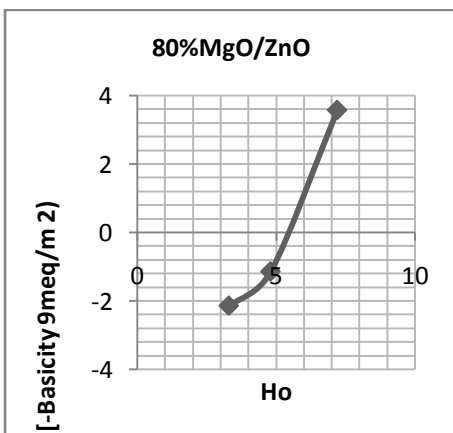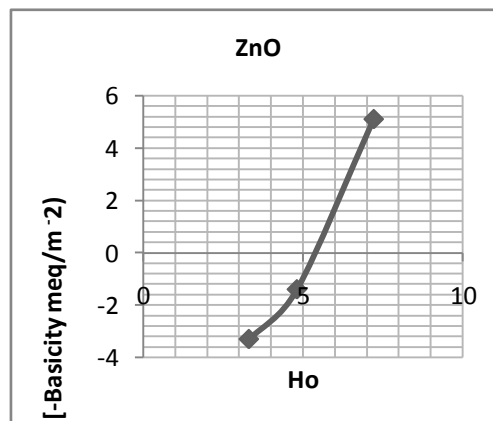Methylene blue showed an absorption maximum at 663nm. Here no decomposition was observed. For MB the % removal was found to be in the following order 20% MgO-ZnO> MgO> 40% MgO-ZnO > 60% MgO-ZnO> 80% MgO-ZnO> ZnO . For 20% MgO-ZnO there is a decrease in absorbance after adsorption. 40% MgO-ZnO is less basic compound compared to 20% MgO-ZnO, but the partice size is larger. Hence cationic MB dye can be properly incorporated on to the 40% MgO-ZnO catalyst surface because the particle size for this system is larger compared to 20% MgO-ZnO and there is a rapid decrease in the concentration of MB. Slight adsorption was found to occur for other oxide systems. No degradation occurs as there is no shift on the absorption maximum and sharp peak was observed without broadness at 663nm.

Since the particle size of MB is less than that of MG ,the high surface area and high basic MgO can adsorb MB to a certain extent. Here 88% decrease of original concentration was observed for MG using 20% MgO-ZnO and 45% decrease was found for MB for the same oxide system. This may be due to smaller size and high electronegativity of +vely charged nitrogen compared to +vely charged sulphur. The %removal of MG and MB using the above oxide system is tabulated in Table VII. For MB and MG using MgO-ZnO, the effect of ultrasound irradiation is eventually detected by the rate of generation of free radicals and other reactive moieties and the degree of contact between the radicals and the contaminants both of which should be maximized. In heterogenous catalytic system, the use of ultrasound creates

Table VIII

Sample	% removal of	
	Malachite Green	Methylene blue
MgO	0	33
20% MgO-ZnO	88	45
40% MgO-ZnO	19	12
60%MgO-ZnO	16	6.4
80%MgO-ZnO	0	3.5
ZnO	0	0

conditions of increased turbulance in the liquid, thus decreasing mass transfer limitations and increasing the surface area available due to catalytic fragmentation and de-agglomeration.

Malachite green a triaryl methane dye is widely used in the aquacultural industry world wide as a biocide as well as in the silk, wool, cotton, leather, paper and acrylic industries as a dye. Furthermore it is employed as a food additive and a medicinal disinfectant. Despite its extensive use, MG is a highly controversial material due to its toxic properties which is known to cause carcinogenesis, mutagenesis, teratogenecity and respiratory toxicity. MG degradation by ultrasound irradiation only has not yet been reported. It was reported that generally the adsorption of organic pollutants follow a Langmuir-Hinshelwood mechanism confirming the heterogenous catalytic character of the system with the reaction rate varying proportionally with the coverage.

Ultrasonication affects the catalyst reactivity during catalysis by enhanced mass-transfer and energy input. In heterogeneous catalysis where the catalyst is in a different phase to the reactants, ultrasonic dispersion increases the surface area available to the reactants. In conclusion, ultrasound irradiation of MgO-ZnO in aqueous solution resulted in significant generation of hydroxyl radicals, and this process may have potential for the treatment of organic dyes in wastewater.

CONCLUSION

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CONCLUSION

 Magnesium-Zinc mixed oxides have found wide commercial application in a variety of industrial chemical processes such as oxidations, reductions and condensations. Though different methods of preparing the catalysts are available in literature, the widely employed co-precipitation method was used for preparing the present mixed oxide systems. On pure MgO strong basic sites consists predominantly of OH^- and O^{2-} anions. The mixed oxides were characterized using FTIR and XRD analysis. All oxide systems are found to be of nano dimensions The mixed oxides are more active due to proper combination of acidic and basic sites. The surface electron properties of oxide systems are found to increase in the following order ZnO<80%MgO-ZnO<50%MgO-ZnO<20%MgO-ZnO<MgO.

The surface acidity and basicity of oxides were also determined by the titration method using Hammett Indicators. The acidic and basic properties of oxide catalysts are very important for the development of scientific criteria in catalyst application. Surface acidic and basic sites of oxides are involved in the catalytic activity for various reactions such as cracking, isomerization, polymerization etc. The base strength of oxide systems was measured as its Ho,max value. The basicity of oxide systems was also found to decrease in the order MgO> 20% MgO-ZnO> 40% MgO-ZnO > 60% MgO-ZnO> 80% MgO-ZnO> ZnO.

When basic sites of Ho≥pka of the indicator exists on a metal surface the surface develops a basic colour and if acid sites of Ho≤pka exists on a solid surface it develops an acidic colour of the indicator. It is assumed that the adsorption equilibrium of both titrant and indicator molecule with acidic or basic sites is assumed on the solid surface . Knowledge of interaction of reactants and products with the surface of a catalyst provides valuable information for a better understanding of a catalytic process. Esterification reaction takes place through the catalyst surface. Surface hydroxyl ions are responsible for electron transfer. Depending upon the exact

condition the holes, OH radicals, O^{2-}, H_2O_2 and O_2 itself can play important role in the photo catalytic reaction mechanism. ZnO is acidic compared to MgO. The presence of MgO in ZnO decreases the acidity of ZnO and also suppresses the activity towards esterification. During esterification n-butyl acetate is formed and analysed using GCMS. Catalytic activity towards desertification was found to be increased in the order ZnO›80%›MgO-ZnO›60%MgO-ZnO›20%MgO-ZnO›MgO. The acidic properties of the catalysts are also in the respective order. Thus we have obtained a good correlation between acid base properties and catalytic activity.

The electron donor properties of MgO can lead to environmental remediation processes. Potential environmental application include sorption and catalytic degradation leading to products that are no longer hazardous. Dyes have long been used in dying paper and pulp, textiles, plastics leather, cosmetics and food industries. Colour stuff discharged from these industries poses certain hazards and environmental problems. Dyes usually have completely aromatic molecular structures which make them more stable and difficult to biodegrade.

Under sonication acoustic cavitation provides a unique interaction of energy and matter and ultrasound irradiation of oxide system and dyes in aqueous solution causes high energy chemical reaction to occur. Of the six oxides systems studied (MgO, 20% MgO-ZnO, 40% MgO-ZnO, 60% MgO-ZnO, 80% MgO-ZnO, and ZnO) 20% MgO-ZnO showed greater adsorption capacity for Malachite green and Methylene Blue from their aqueous solutions, may be due to proper combination of basicity and particle size.

The sonication using nano dispersion is a better method to remove waste water pollutants. The result showed that availability of negatively charged groups at the adsorbent surface is necessary for the adsorption of basic dyes to proceed. For pure MgO the particle size becomes finer as determined from XRD. But for 20% MgO-ZnO the particle size and basicity are of correct dimension for greater adsorption of

MG and MB. Here 88% of decrease in original concentration of MG was observed for 20% MgO-ZnO and 45% decrease for MB.

N-demethylation was also occurred for malachite green as observed from the colour difference and broadness of the UV absorption peak for 20% MgO-ZnO. No degradation but only adsorption for MB on 20% MgO-ZnO. Thus oxide ion system provide stable catalytically active site for reaction to occur compared to pure oxides. Greater activity was observed for MG compared to MB. For MG sonocatalytic activity was found to decrease in the order: 20% MgO-ZnO > 40% MgO-ZnO > 80% MgO-ZnO but for MB the above decrease was found to be in the order 20% MgO-ZnO> MgO> 40% MgO-ZnO > 60% MgO-ZnO> 80% MgO-ZnO> ZnO . A considerable amount of research is being devoted to the wide spectrum of biological effects it exerts on different animals and on mankind. There is concern about MG and its reduced form Leucomalachite green in aquatic and terrestrial ecosystem science. They occur as contaminants and are potential human health hazards.

Here the acid base properties parallel the surface electron properties and catalytic activity of the Mg-Zn mixed oxide systems.

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