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Catalytical and Luminscence properties of Magnesium Oxide and its Composite

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Abstract : Chemical co precipitation is a simple technique to synthesize oxides and composite oxides. In the nano regime the increased surface area per volume contributes to the exotic properties exhibited by them especially where surface area plays main role. Magnesium oxide, and (Zn/Mg) oxides are synthesized by precipitation technique followed by thermal reduction. Optical properties by UV Visible absorption and PL Studies. Catalysis activity in esterification is also probed. period.

***Key Words*:**nano metal oxides,band gap,composites,esterification,luminescence.

1. INTRODUCTION

The field of nanotechnology is one of the most active areas of research in modern materials science. New applications of nano-particles and nano-materials are emerging rapidly. Nano crystalline particles have found tremendous applications in the field of high sensitivity bio molecular detection and diagnostics, antimicrobials and therapeutics, catalysis and microelectronics [1]. Nanometre-sized clusters themselves possess several unusual and potentially useful properties in this regard. These include unusually high surface areas, a high degree of geometrical surface defects, enhanced nonlinear optical properties, and electronic and therefore chemical reactivity properties which are inherently different from both their corresponding atoms and molecules and from their bulk forms. Likewise, consolidated nanophase materials also exhibit properties different from those of conventional bulk materials.

To maximize activity, it is desirable to utilize catalysts with very high surface areas since the critical step in this process appears to occur at the surface. Given their intrinsically high surface areas, unsupported nano-particles of mixed metal oxides are particularly well-suited for this purpose. The only alternative high surface area catalysts are molecular sieves such as zeolites and supported nano-particles, the former being inappropriate for this application and the latter exhibiting smaller active surface areas per mass than unsupported nano-particles. Conventional metal oxide catalysts typically possess surface area-to-mass ratios on the order of 1 m2/g (typical particle diameters of ~1 µm). For spherical particles, this ratio should scale as ~D-1, where D is the particle diameter. The size regime of nanophase particles lies between the particle sizes of conventional oxidation catalysts and those of isolated atoms and molecules. Within this size regime, D can vary over three orders of magnitude, yielding surface area-to-mass ratios up to about three orders of magnitude larger than conventional catalysts. With such high surface areas, nanometre particles may display significantly enhanced activities over conventional catalysts. In addition to this surface area effect, other intrinsic properties of nanodimensional particles may make them desirable catalysts. The large number of surface geometrical defects in these systems may have important effects on catalytic selectivity, and their unique electronic properties may lead to attractive reactivity characteristics for these particles.

Synthesis:

The chemicals are purchased from MERCK and are used without further purification. Freshly prepared aqueous solutions of the chemicals are used for the synthesis of nano particles.The solutions of Magnesium Acetate , Zinc acetate and Ammonium Carbonate were prepared in distilled water for 0.05 M,. EDTA was used to prevent agglomeration and sodium hydroxide to control pH. The molar concentration of EDTA and Sodium Hydroxide were optimized as a compromise between yield and particle size. After slow addition and continuous stirring the carbonate precipitate was filtered, dried and annealed to obtain oxides

2. Characterization and Results

3.1 Structural studies

The structural characterization was done using XRD and SEM. The results obtained show the formation of nanoparticles of oxides and its composites are pure and doesn't contain carbonate other mother reagents

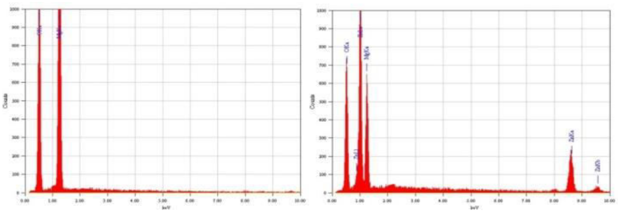

Figure1. EDS of MgOand(Zn/Mg)O

SEM micrographs (figure 3) show the formation of nanoflakes of magnesium oxide. The SEM micrograph of composite oxides show homogeneous nature. The TEM micrographs confirms the nano sized oxides in at least one dimension.

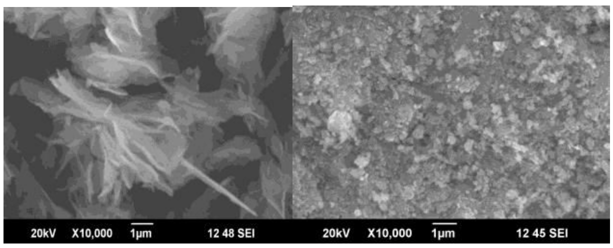

Figure 2.SEM micrographs of MgO and (Zn/Mg)O

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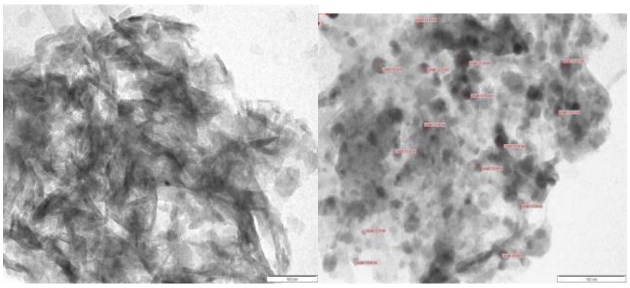


Figure 3. TEM micrographs of MgO and (Zn/Mg)O

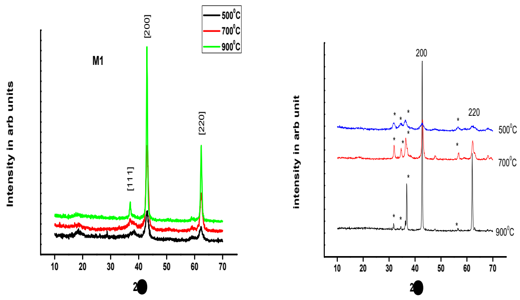


Figure 4. XRD patterns of MgO and (Zn/Mg)O

Table 3.8 The comparison of values obtained from XRD with the reported values (JCPDS Card No 87-0653) of Magnesium Oxide nanoparticles

2θ(Degrees)	Interplanar distance(A^0)		h,k,l	Lattice constant $a(A^0)$	Rel. intensity of peaks	
	d_{observ} d.	d_{jcpds}			observed	Jcpds
36.96	2.430	2.424	111	4.209	11.95	11.5
43.09	2.097	2.1	200	4.194	100	100
62.34	1.488	1.48	220	4.208	44.68	45.1

The peaks marked by * in the patterns of composite (figure 4 (b)) corresponds to that from Zinc Oxide. The intensity of the peaks corresponding to that from Magnesium Oxide is found to be a maximum. The EDAX also shows increased percentage of magnesium in these samples. The particle sizes of the prepared samples and the samples sintered at different temperatures are calculated using Debye –Scherrer equation [2 ,3].

The slight change in the d-values can be attributed to the nano sized species of this mixed oxide. The XRD peaks are broadened due to the nano crystalline nature of the particles. These nano crystals have lesser lattice planes compared to the bulk, which contributes to the broadening of peaks in the diffractogram. This broadening of the peaks could also arise due to the micro straining of the crystal structures arising from defects like dislocations, twinning etc. These are believed to be associated with the chemically synthesized nano crystals as they grow spontaneously during chemical reaction. As a result, chemical ligands get negligible time to diffuse to an energetically favourable site. It could also arise due to lack of sufficient energy needed by an atom to move to a proper site in forming the crystallite [4]Warad et al 2005]. As the particle size decreases the width of the diffraction peak increases and hence the broad peak is a characteristic of a nanoscopic material [5,6,7,8].

Table 2 The lattice parameters obtained for the (ZnO/MgO) nano composite in comparison with JCPDS values . [ZnO - JCPDS Card NO 75-0576, MgO- 77-2364

2θ(Degrees)	**Interplanardistnces 'd'(A^0)**		**h,k,l**	**Rel intensity of peaks**	
	d_{observ} d	**d_{jcpds}**		**Observed**	**JCPDS**
32.05	2.79	2.81	100	64.01	56.16
34.77	2.57	2.59	002	48.81	41.24
36.55	2.456	2.47	101	100	100
43.06	**2.09**	**2.10**	**200**	**100**	**100**
47.90	1.897	1.907	102	14.76	21.52
56.85	1.618	1.621	110	32.55	30.9
62.35	**1.488**	**1.488**	**220**	**45.53**	**45.1**
63.27	1.469	1.474	103	22.87	27.23
66.55	1.404	1.404	200	4.14	4.1
68.24	1.373	1.375	112	20.92	22.72
69.35	1.354	1.355	201	11.2	10.6

2.2 Optical Studies:

Optical absorption and emission studies are done using UV – Visible spectroscopy and photo luminescence studies.The optical conductivity is one of the fundamental properties of metal oxides and can be experimentally obtained from reflectivity and absorption measurements. Due to quantum-size confinement, absorption of light becomes both discrete-like and size-dependent. For nano-crystalline semiconductors, both linear (one exciton per particle) and non-linear optical (multiple excitons) properties arise as a result of transitions between electron and hole discrete or quantized electronic levels.

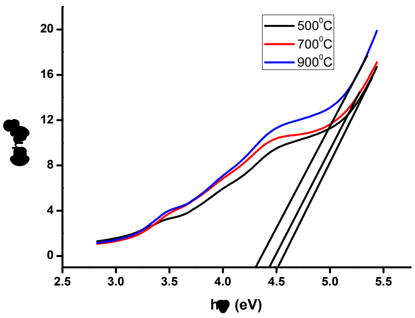


Figure Tauc Plots ofMgO

From the absorption data band gap of materials are calculated using Tauc plots. The band gap is found to be varied from the bulk values due to confinement.The band gap of annealed nanoparticles of sample MgO at temperature 300^0C is 4. 5 eV which further reduced to 4.29 eV when annealing temperature increased to 900^0C.

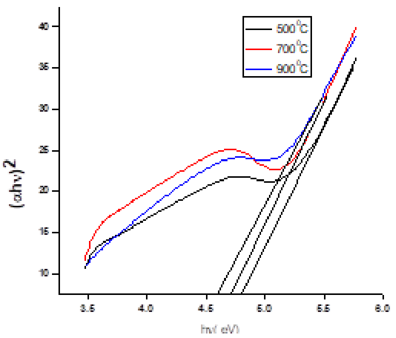
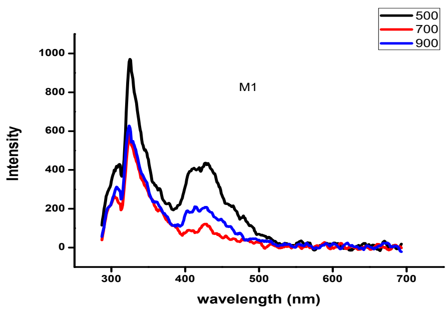


Figure Tauc Plots of(Zn/Mg)O

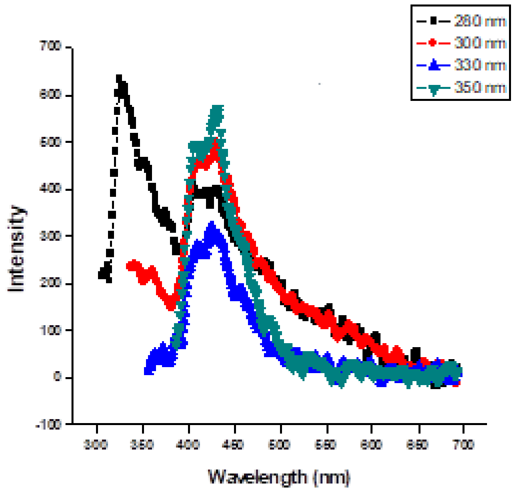
Luminescence in solids is the phenomenon in which electronic states of solids are excited by some energy from an external source and the excited states release energy as light. When short-wavelength light illuminates a solid and result in the emission of higher wavelength, the phenomenon is called photoluminescence (PL) [9]. PL is divided into two major types: Intrinsic and extrinsic depending on the nature of electronic transition producing it.



Pl Spectra of MgO

The excitation wavelength is 250 nm and there are two peaks in the spectrum of MgO, one between 320-350nm and another between 410-450 nm. The emission in the 320 range is sharp but the other peak is very broad. This emission can be attributed to the displacement of oxygen ions and subsequent electron trapping resulting in the formation of F centres [10]. The dependence of emission on the excitation wavelength is also probed and it is seen that the sharp emission at 325 nm disappears with increase in the excitation wavelength to 300 nm and the band at 430 nm became sharper with a corresponding increase in intensity. The inefficient energy transfer between the upper and the lower vibrational levels of the excited state of these particles owing to short fluorescence lifetime is primarily responsible for the excitation wavelength dependent spectral shift of Magnesium Oxide colloids.

The luminescence spectra also changed with annealing temperature. Here the intensity of both peaks is found to decrease with increase in temperature.



PL spectra of (Zn/MgO)

The emission of composite also showed excitation wavelength dependence. The emissions from the composite in the 400-450nm region decreased on increasing the excitation wavelength.The emission at 320 nm was present only for excitation wavelength 280 nm.

2.3 Catalyst in esterification

Due to environmental concerns, the major trend in the field of catalysis is to find newer catalysts, which are environment friendly. Various solid state acid catalysts like zeolites, sulphated zirconia, clay minerals are being explored for industrially important reactions. A major drive for developments in the field of surface science has been fuelled by the desire to achieve a thorough fundamental understanding of the adsorption mechanisms involved in heterogeneous catalysis and hence the catalytic activity [11].

The esterification reaction is widely used in the chemical reaction process to form ester. Esterification is an industrially important reaction for synthesis of drug intermediates, polymer processing additives, dye stuff and fine chemical intermediates. The conventional catalyst used in esterification reactions is sulphuric acid cited as a potential environmentally hazardous chemical, posing several disadvantages in industrial processes, which include wasting large amount of catalyst, corroding reactors, causing acidic waste water, difficulty of catalyst recovery etc. In view of the deficiencies encountered, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids. They possess high catalytic activity and selectivity, do not corrode reaction vessels or reactors and finally can be used repeatedly. Manohar et al [12] have reported the use of ZrO_2 impregnated with molybdenum and tungsten as solid acids for esterification reactions.

Table 3.Esterification results

Acid:Alcohol	Weight of catalyst in gm.	Time in hrs.	% Yield (ZnO/MgO)	% Yield MgO
1:1	0.1	1	60.17	64.86
1:1	0.1	2	61.95	75.22
1:1	0.3	1	61.95	75.22
1:1	0.3	2	63.72	87.29
1:1	0.5	1	69.91	89.83
1:1	0.5	2	71.68	90.27
1:1	1	1	80.53	93.64
1:1	1	2	83.19	97.46
2:1	0.1	1	66.53	77.97
2:1	0.1	2	69.92	86.86
2:1	0.3	1	72.04	87.29
2:1	0.3	2	73.73	89.83
2:1	0.5	1	84.32	80.27
2:1	0.5	2	87.29	95.33
2:1	1	1	88.98	96.61
2:1	1	2	91.01	98.23

The acid sites on metal oxides are believed to be ascribed to surface hydroxyl groups or a charge imbalance localized on the surface. Localization of deficient amounts of electrons results from a local imbalance between positive and negative charges of the constituents and act as a Lewis acid for catalytic reactions. Since a charge imbalance can be expected by substituting the metal ion with other metal ions possessing different charges, new acid sites could be designed on the surface of doped and or mixed metal oxides [13,14,15]. The features, acidity and surface area, make many of these super acid compounds very active as catalysts when used in reactions that generally are catalysed by strong acids. A similar enhancement in catalytic activity is also shown by non-metal sulphated materials [16]. According to Salmones*et al.*, the enhanced catalytic properties of platinum are improved by using a sulphated mixture of silica and zirconia as support.

In the present work the catalytical activity of metal oxide and its composite metal oxide namely MgO and (ZnO/MgO), in esterification process is investigated. As a model reaction, formation of ester from acetic acid and ethylene glycol is studied varying quantity of catalyst, time of reflux and acid, alcohol ratio. The catalytical activity of the individual metal oxides and mixed metal oxide form are studied separately in the esterification reaction of ethylene glycol with acetic acid. The ratio of the acid: alcohol as well as reaction time are varied and found that these nanoparticles are very effective as catalysts. The variation in the yield with concentration and time are given in Table 3.

3. CONCLUSIONS

The structural,morphological and optical properties of magnesium oxide nanoparticles and its composite with zinc is analysed. The use of these metal oxides as phosphors and catalyst in esterification process are studied in detail and the result obtained are discussed. .

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