Synthesis and Characterization of MnO_2/MgO Nano sheets: An efficient Recyclable Solid Base to Wittig Reaction

M. H. Moulavi
Department of Chemistry, PDEA's Annasaheb Waghire College, Otur, Pune 412409

Abstract

Surface modification of MgO solid base is an important task in order to carry organic reaction for pollution free environment. For this purpose, MnO_2/MgO mixed oxide nanosheets are prepared by alkali leached hydrothermal method at 150 ^{O}C for 48 hrs. As synthesized corresponding hydroxides are calcined at 450 ^{O}C for 6 hrs to form mixed MnO_2/MgO oxide. Mixed oxides are characterized by XRD, UV-DRS, IR, FESEM and EDS Analysis. XRD revealed formation of tetragonal crystal structure MnO_2 mixed with cubic crystal system of MgO. FESEM shows formation of nanosheets of 20 nm thickness. Prepared mixed MnO_2/MgO nanosheets are used as solid recyclable base in Wittig reaction of benzaldehyde and phosphonium salt in DMF solvent at room temperature. Recycling of solid base is associated with no change in crystal phases and purity of materials. Surface activity after comparison with nanocrystalline MgO shows that higher valent Mn is responsible for enhancing surface basicity of MgO.

Key Words: MnO_2/MgO nanosheets, Wittig reaction, surface basicity.

1. Introduction:

Nanostructured metal oxides are identified for their versatile applications in organic synthesis [1]. Solid nature of such heterogenetic metal oxide able chemists to carry out organic reaction in an economic way for pollution free environment due to recyclability and reusability nature. In organic synthesis, vast number of base mediated organic reactions are known. Among such base mediated organic reactions, Wittig reaction is well known for synthesis of alkene from aldehyde or ketones. Utilization of strong, excessive basic condition and unwanted separation diverts chemists from Wittig reaction unless some selectivity is expected in olefin synthesis. At industrial scale, Wittig reaction is adopted for synthesis of vitamin A, fragrances and important drugs. Ethyl cinnamate is such important alpha, beta unsaturated ester synthesized by Wittig reaction and utilized as flavoring agent [3]. Broad applicability of Wittig reaction attracted the chemists for synthesis of ethyl cinnamate under heterogeneous basic condition. Different solid bases such as ZnO, MgO, hydrocalcites etc. are utilized in Wittig reaction, but less reactivity of pure solid bases limited the use in Wittig reaction at industrial scale. MgO is very popular solid base used in most of base catalyzed organic reaction [4]. Nanocrystalline MgO is used in Wittig reaction [5]. It is well known that, surface basicity of MgO is due to different low coordinated surface oxygens, known as active basic sites. The number and coordination nature of surface basic sites decides the overall reactivity and hence basicity of MgO system [6]. With this study attempts were going on to modify the surface basicity of MgO by controlling basic sites. Under normal condition, MgO takes longer reaction time for synthesis of ethyl cinnamate by Wittig reaction and activation of MgO at higher temperature is major drawback. To some extent, surface activity of MgO can be modified by formation of mixed metal oxides like ZnO/MgO [7]. Such low valent metal oxides with MgO necessitate use of very bulk amount. Use of larger quantity of this mixed oxide associated with very poor yield. La/MgO assisted Wittig reaction shows very lengthy reaction time [8].

Higher oxidation state of metals in mixed oxide shows impact by surface basicity enhancement and it operates reversibly in organic reaction due to acidic and basic interaction [9]. So both effects result for use of catalytic amount of solid base and short reaction time. Distortion of crystal structure of MgO is more beneficial with higher oxidation Mn than low valet metal oxides. Surface basicity of metal oxides can be controlled by method of preparation and preparation conditions. With this view, hydrothermal method found to be very useful and simple method for preparation of mixed metal oxides [10]. Alkali leached hydrothermal method is useful for preparation of mixed metal oxides with different morphology and hence expected surface reactivity of basic systems can be achieved.

With this view, MnO_2/MgO nanosheets are prepared by alkali leached hydrothermal method and used as recyclable solid base in Wittig reaction of benzaldehyde and phosphonium salt.

2. Experimental:

For preparation of MnO_2/MgO nanosheets- $MnCl_2.4H_2O$, NaOH flakes etc. and for Wittig reaction- benzaldehyde, triphenyl phosphine, DMF, Ethyl acetate, toluene, hexane solvent etc. chemicals are purchased from Loba Chemicals. XRD analysis of materials is performed using Bruker AXS model D-8. FESEM analysis is performed over HITACHI, S-4800 model. UV-DRS is determined by using Scimadzu UV-3600 instruments. Elemental composition is analysed by EDS on Bruker XFlash 6130 instruments. For Wittig reaction phosphonium bromide is prepared by reaction between ethyl bromoacetate and triphenyl phospine in toluene solvent in quantitative yield using reported procedure.

2.1 Preparation of MnO_2/MgO nanosheets by alkali leached hydrothermal method.

For preparation of alkali leached MnO_2/MgO mixed oxides by hydrothermal methods, 5.O gm of commercial MgO and 0.918 gm $MnCl_2.4H_2O$ is leached 10 M 100 ml NaOH in 200 ml hydrothermal reactor for 48 hrs at 150 ^OC. The resulting hydroxide is dried at 60 ^OC for 6 hrs. After calcination at 450 ^OC, it yields MnO_2/MgO nanosheets as confirmed from FESEM analysis. Same procedure was followed for preparation of pure undoped nanocrystalline MgO without addition of salt precursor.

2.2 *Wittig reaction of phosphonium salt with benzaldehyde in presence of MgO and MnO_2/MgO mixed oxides*.

For preparation of ethyl cinnamate by Wittig reaction, 4.6 mmol of phosphonium salt is stirred with 6.9 mmol benzaldehyde in presence of solid base in 5 ml DMF solvent. Reaction is monitored by TLC. After disappearance of reactant, ethyl acetate is added and content was transferred to separating funnel solid base is separated by centrifugation. The resulting content is separating funnel is worked up with water to remove DMF solvent. After separation of products from solvent and catalysts, ethyl acetate extract was dried over anhydrous sodium sulphate and evaporated under vacuum.

Further, products and byproducts are separated by column chromatography using pure hexane as eluent. The resulting liquid ethyl cinnamate is characterized by IR, 1H-NMR and HR-MS.

3. Result and Discussion:

In proposed research work, MgO2/MgO mixed oxides are prepared by alkali leached hydrothermal method and used as solid recyclable base in Wittig reaction between phosphonium bromide salt and benzaldehyde. Surface basic activity is compared with pure nanocrystalline MgO. The as synthesized material is characterized by XRD, UV-DRS, IR, FESEM and EDS Analysis.

3.1 Characterization of pure nanocrystalline MgO and MnO_2/MgO mixed oxides.

3.1.1 XRD analysis

Figure1 represents the XRD pattern of hydrothermally prepared nanocrystalline $Mg(OH)_2$ (Fig 1a) and calcined nanocrystalline MgO (Fig. 1b) and MnO_2/MgO mixed oxide (Fig. 1c). When commercial MgO is subjected to alkali leached hydrothermal condition, it is converted to corresponding hydroxide. XRD analysis of resulting magnesium hydroxide (Fig. 1) shows 2θ values at 18.52, 32.89, 37.99, 50.86, 58.63, 62.05, 68.32 for 001, 100, 101, 102, 110, 111, 103, 201 planes respectively. Such 2θ values with corresponding plane indicates hexagonal crystal system with brucite phase (JCPDS file no 44-1482). After calcination of hydroxide at 450 ^OC it decomposes to nanocrystalline MgO. The resulting oxide shows 2θ values 36.91, 42.88, 62.29, 74.68, and 78.61^O for 111, 200, 220, 311, 222 planes respectively (Fig. 2b), indicating formation of simple cubic system with periclase phase (MgO (JCPDS file no 45-0946). Same procedure was followed for preparation of MnO_2/MgO mixed oxide by addition of salt precursor. XRD analysis of mixed oxides (Fig.1c) shows 2θ values at 18, 28, 36 and 58^O with MgO crystal planes corresponding to of tetragonal body centered α-MnO_2 (JCPDS file 44-0141). Overall XRD analysis revealed that MnO_2 tetragonal crystal phase is mixed with simple cubic phase of MgO.

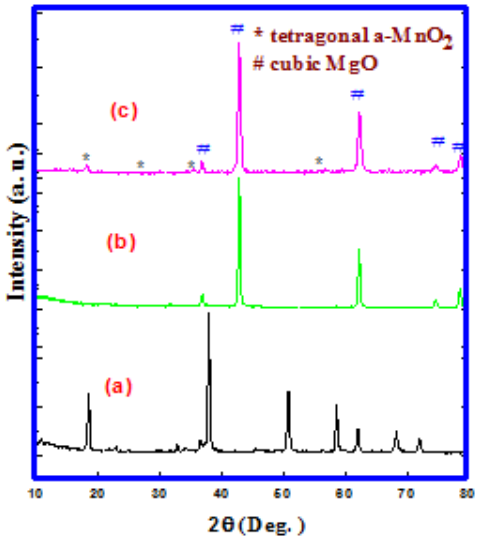


Figure 1. XRD analysis of (a)$Mg(OH)_2$ (b)nanocrystalline MgO (c) MnO_2/MgO

3.1.2 UV-DRS analysis

Figure 2 represents the UV diffused absorption spectra of pure nanocrystalline MgO and MnO_2/MgO mixed oxides. Nanocrystalline MgO shows formation of pure phase with absorption band around 274 nm only (Fig. 2a). In case of MnO_2/MgO mixed oxides, two sharp absorption bands at 228 nm and 275 nm are observed. The absorption bands in MgO are associated with electronic excitation of low coordinated oxygen ions on surface. In this bands 274 nm represents the 3 coordinated oxygen excitation while 228 nm represents 4 coordinated oxygen's excitation [11]. Overall UV-diffused absorption study indicates that MnO_2/MgO surface is more populated with 3 and 4 coordinated oxygen's than pure nanocrystalline MgO reasoning for increasing surface basicity. The absorption band at 420 nm attributed to presence MnO_2 in sample [12].

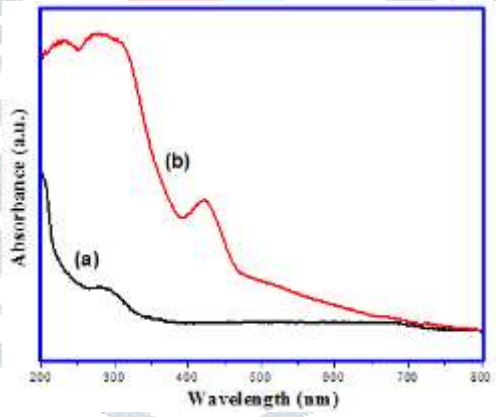


Figure 2 UV-diffused absorption analysis of (a) Nanocrystalline MgO (b)MnO_2/MgO

3.1.3 FT-IR analysis.

Figure 3 represents FT-IR spectrum of nanocrystalline MgO and MnO_2/MgO mixed oxide. For nanocrystalline MgO (Fig. 3a) different absorption bands located between 400-850 cm^{-1} which are attributed to different coordinated Mg-O stretching vibrations. In first region in 400-500 cm^{-1} fundamental bands are observed [13], while in second region 550-850 cm^{-1} combination bands of fundamental stretching frequencies are seen 14]. IR bands appearing between 1400-1600 cm^{-1} and between 4300-3600 cm^{-1} are attributed to chemisorption of CO_2 and water on surface of MgO respectively [15].

In case MnO_2/MgO mixed oxides the broad combination bands are replaced by bands of O-Mn-O bands in MnO_2 sample [16]. In region 400-500 cm^{-1} IR region different Mn-O and Mg-O stretching vibration peaks are appeared suggesting for presence of MnO_2 mixed with MgO.

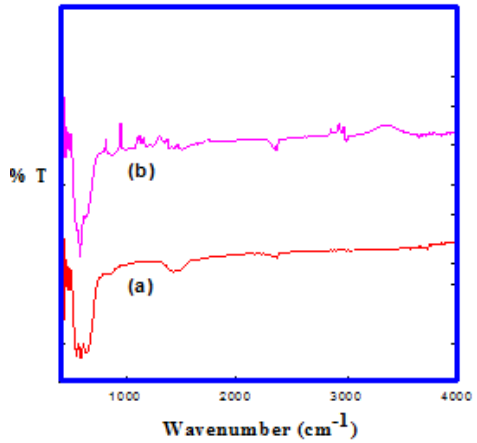


Figure 3 FT-IR analysis of (a)Nanocrystalline MgO (b)MnO_2/MgO

3.1.4 FESEM Analysis.

Figure 4 shows the FESEM images of nanocrystalline MgO and MnO_2/MgO mixed oxides. FESEM analysis for nanocrystalline MgO (Fig 4A) shows the formation hexagonal plates with 32 nm thickness under the alkali leached hydrothermal method. Under the same condition addition, Addition of Mn precursor salt in MgO shows formation of nanosheets with 20 nm thickness (Fig. 4B). The particles size is well agreement with calculated by Scherer's equation for XRD peaks.

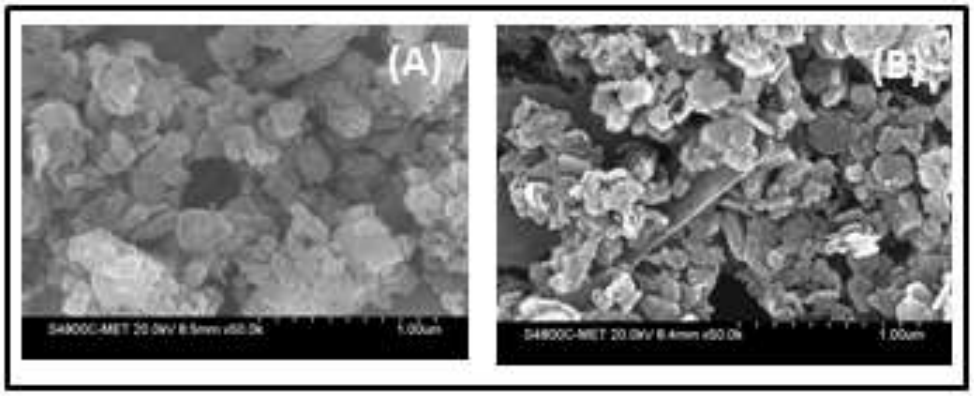


Figure 4 FESEM analysis of (a-b) Nanocrystalline MgO (c-d) MnO_2/MgO

3.1.5 EDS analysis:

Figure 5 shows elemental analysis of 5 % MnO_2/MgO mixed oxide nanosheets by EDS analysis. The EDS analysis of prepared sample by EDS analysis shows presence of Mg, O and Mn elements in mixed oxides. The expected elemental composition of Mn was found to be 4.73 %.

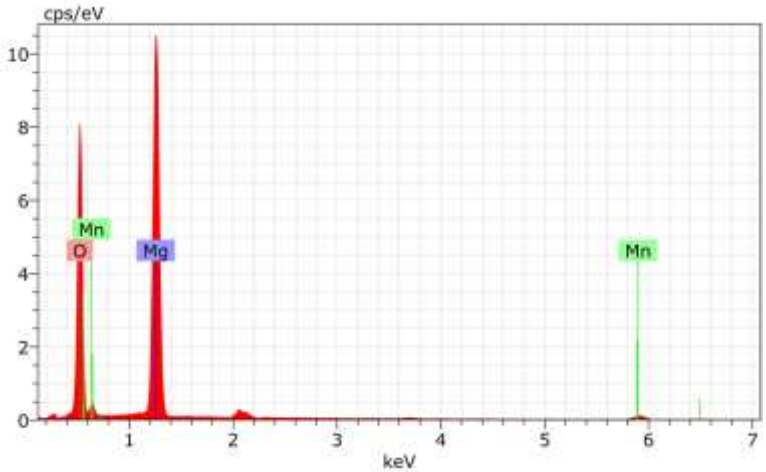
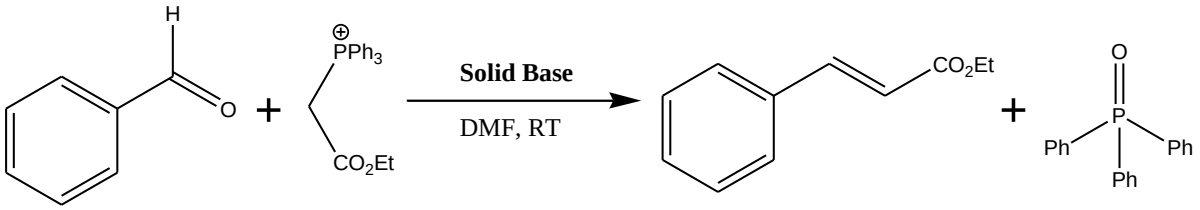


Figure 5: Elemental Analysis of 5 % MnO2/MgO oxide

The characterization by XRD, UV, IR, FESEM and EDS analysis suggested the 5 % MnO_2/MgO mixed oxide with nanosheets morphology.

3.1.6 Basic activity measurement:

The nanocrystalline MgO and MnO_2/MgO nanosheets prepared by alkali leached hydrothermal method and used as solid recyclable base in Wittig reaction between phosphonium salt and benzaldehyde in DMF Solvent. For measurement of surface basic activity of 10 wt% of each solid base was stirred in presence of 4.6 mmol of phosphonium bromide salt with 4.6 mmol of benzaldehyde in 5 ml DMF solvent **(Scheme 1).** The catalytic activities of two different MgO solid bases are compared. All solid bases are activated by heating at 700 ^{O}C prior to use in reaction.



Scheme 1. Wittig reaction in presence of different MgO based solid base.

Table 1. basic activity of nanocrystalline MgO and MnO_2/MgO solid base.

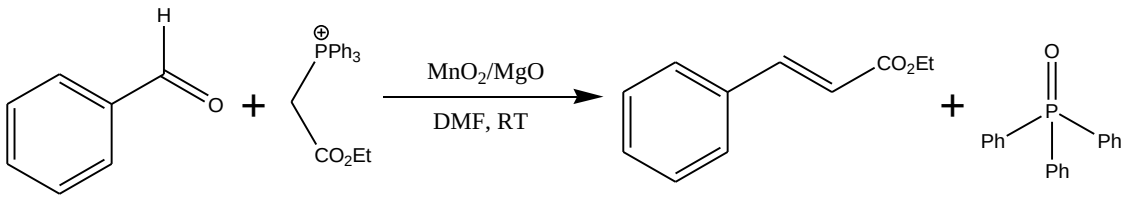
No	Solid Base	% yield
1	Blank reaction	0
2	Commercial MgO*	45
3	Commercial MgO	60
4	Nanocrystalline MgO	72
5	MnO_2/MgO	81

Reaction condition: 10 wt% of each solid base activated is stirred with reactants in 5ml DMF solvent at RT.
*without heating

From table 1, it is evident that MnO_2/MgO solid bases are more basic over nanocrystalline MgO than commercial MgO and nanocrystalline MgO due to higher oxidation of Mn [17] and surface defects on surface of MgO. Basicity of each solid base is effective only when catalysts is activated by heating. Heating required for elimination of CO_2 and water vapors to expose the basic sites. Further to get quantitative yield of product ethyl cinnamate, reaction is optimized for reactants and catalysts amount.

3.1.7 Optimization of reactant amount.

For optimization of reactant amount, the concentration of benzaldehyde varied from 1 to 1.5 equivalents, it shows positive effect (Fig. 6a) on basic activity of solid base, while increasing concentration of phosphonium salt from 1 to 1.3 equivalents, it shows negative effect (Fig. 6b) on basic activity of solid base. On decreasing base amount from 10 wt% to 2.5%, best results (Fig. 6c) are obtained at 5wt% of MnO_2/MgO with respect to 4.7 mmol of phosphonium salt. So reaction is optimized at 1.5 equivalent (6.9 mmol) benzaldehyde with 4.7 mmol phosphonium salt in presence of 5wt% MnO_2/MgO nanosheets as a solid base. So under optimized reaction condition for 5 wt% solid base MnO_2/MgO shows 90 % yield of ethyl cinnamate (Scheme 2)



Scheme 2. Wittig reaction in presence of different MnO_2/MgO nanosheets.

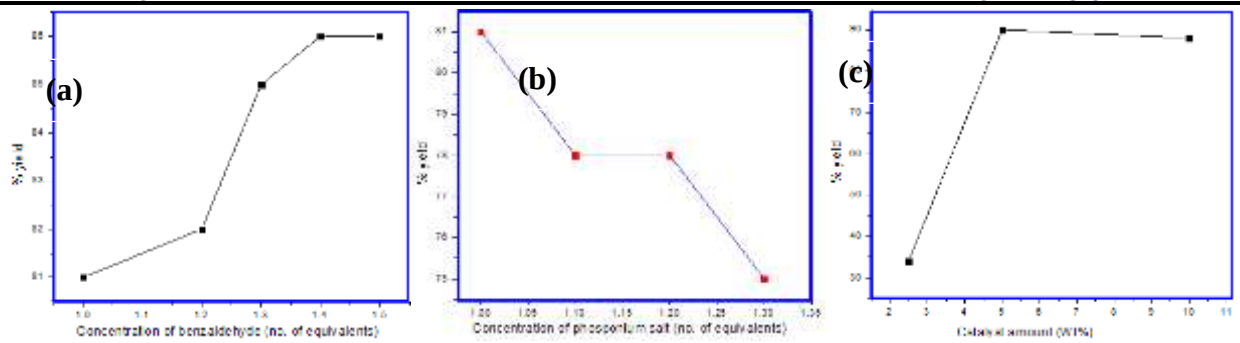


Figure 6. Effect of concentration of (a)benzaldehyde, (b)phosphonium salt and (c)catalysts amount of basic activity of MnO_2/MgO.

3.1.7 Recycling of MnO_2/MgO.

After optimization of Wittig reaction for reactant quantity and base amount, it is evaluated for recycling because of solid nature. After first cycle, the solid base is separated by centrifugation. After first cycle 96 % of solid base is recovered for next cycle. Recovered base is again characterized by XRD. The XRD after first cycle shows same purity and crystal phase. In this way use of solid recyclable 5 wt% MnO_2/MgO mixed oxide in Wittig reaction is economic and pollution free.

4. Conclusion:

The MnO_2/MgO nanosheets prepared by alkali leached hydrothermal methods are more basic over the nanocrystalline MgO due to higher oxidation state of Mn and increased number of low coordinated oxygen on surface. Under the optimized reaction condition in Wittig reaction, MnO_2/MgO mixed oxides shows 90 % basic activity. The reported methodology is economic, pollution free and easy to scale up.

5. Acknowledgement:

Authors are very thankful to Dr. B. B. Kale, Nanocrystalline Lab (C-MET, Pune) for characterization facilities and UGC final financial support in the form of Minor research Project.

Characterization of Wittig product:

The Wittig product ethyl cinnamate is characterized by HR-MS and ^{1}H-NMR.

1)HR-MS: (Mol. Formula $C_{11}H_{12}O_2$)
[M+H] ion for 177.09. (For $C_{11}H_{13}O_2$)

2)^{1}H-NMR (500 MHz, $CDCl_3$) for E-ethyl cinnamate

1.3 ppm (triplet, 3H, J=7.5 Hz), 4.25 ppm (quartet, 2H, J=7.5 Hz), 4.26 ppm (doublet, 1H, J= 16 Hz, 7.34 ppm (triplet, 3H, J=3.5 Hz), 7.48 ppm (quartet, 2H, J=3.5 Hz), 7.67 ppm (doublet, 1H, J=16 Hz).

6. References:

1. Manoj B. Gawande, Rajesh K. Pandey, Radha V. Jayaram, Role of mixed metal oxides in catalysis science—versatile applications inorganic synthesis, *Catal. Sci. Technol*., 2012, 2, 1113–1125.
2. Pommer H., Thieme P.C. (1983) Industrial applications of the wittig reaction. In: Wittig Chemistry. Topics in Current Chemistry, vol 109. Springer, Berlin, Heidelberg.
3. S.P. Bhatia, G.A. Wellington, J. Cocchiara, J. Lalko, C.S. Letizia, A.M. Api, Fragrance material review on ethyl cinnamate, *Food and Chemical Toxicology* 45 (2007) S90–S94.
4. Boyapati M. Choudary, Kalluri V. S. Ranganath, Ujjwal Pal, Mannepalli L. Kantam, and Bojja Sreedhar, Nanocrystalline MgO for Asymmetric Henry and Michael Reactions. *J. Am. Chem. Soc.*, 2005, *127* (38), pp 13167–13171.
5. Moulavi Mansur, Kanade Kaluram, Arbuj Sudhir, Kale Bharat, Comparative Study of Surface Activation of Nanocrystalline MgO Under Thermal and Microwave Heating in Wittig Reaction. *Int. Res. J. of Science & Engineering*, *2018A*3 : 28-34.
6. Elizabeth Florez, Patricio Fuentealb, Fanor Mondrago, Chemical reactivity of oxygen vacancies on the MgO surface: Reactions with CO_2, NO_2 and metals, *Catalysis Today*, 133–135 2008,216-222.

7. Helène Moison, FrançoiseTexier-Boullet. Andre Foucaud, Knoevenagel, wittig and wittig-horner reactions in the presence of magnesium oxide or zinc oxide. *Tetrahedron*, 43(3), 1987,537-542.
8. M. L. Kantam, K. B. S. Kumar, V. Balasubramanyam, G. T. Venkanna, F. Figueras, One-pot Wittig reaction for the synthesis of alpha, beta-unsaturated esters using highly basic magnesium/lanthanum mixed oxide. *Journal of Molecular Catalysis A Chemical* 321(1) 2010:10-14.
9. By D. Cordischi, R. L. Nelson, A. J. Tenc. B. Surface Reactivity of Magnesium Oxide doped with Manganese: an E.S.R. and Chemisorption Study, *Trans. Faraday Soc.* **,**65**,** 1969, 2740-2757.
10. G.G. Nakhate, V. S. Nikama, K. G. Kanade, S. Arbuj, B. B. Kale, J. O. Baeg, hydrothermally derived nanosized Ni-doped TiO2: A visible light driven photocatalyst for methylene blue degradation, *Materials Chemistry and Physics*, 124(2–3), 2010, 976-981.
11. Minhua Zhang, Meixiang Gao, Jianyue Chena and Yingzhe Y, Study on key step of 1,3-butadiene formation from ethanol on MgO/SiO2, *RSC Adv.*, 5,2015, 25959.
12. Reenu Elizabeth John, Anoop Chandran, Marykutty Thomas, Joshy Jose K C George, Surface-defect induced modifications in the optical properties of α-MnO2 nanorods. http://dx.doi.org/doi:10.1016/j.apsusc.2016.01.153.
13. C. V. Raman, 1947. The vibration spectra of Crystals-Part IV. Magnesium oxide. *Proc. Indian Acad. Sci. A.* 26(1947), 383-390
14. C. V. Raman. The vibrations of MgO crystal structure and its infrared absorption spectrum. *Proc. Indian Acad. Sci. A.* 54(1961). 205-222.
15. R. Philippt, K. Fujimoto. FTIR spectroscopic studies COP adsorption/Desorption on MgO/CaO catalysts. *J. Phys. Chem*. 96(22), 1992, 9035-9038.
16. Deogratius Jaganyi, Mohammad Altaf ,Isaac Wekesa, Synthesis and characterization of whisker-shaped MnO2 nanostructure at room temperature, *Appl Nanosci*, 3(4), 2013, 329–333.
17. Fernando Stavale, Xiang Shao, Niklas Nilius, Hans-Joachim Freund, Stefano Prada,Livia Giordano, Gianfranco Pacchioni, *J. Am. Chem. Soc*. 134, 2012, 11380−11383.