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Comparative Study of Surface Activation of Nanocrystalline MgO Under Thermal and Microwave Heating in Wittig Reaction

Moulavi Mansur[1,2], Kanade Kaluram[1,3*], Arbuj Sudhir[1], Kale Bharat[1]

[1]Centre for Materials for Electronics Technology (C-MET), Panchwati, Off Pashan Road, Pune 411008, India. [2]P.G. Department of Chemistry, PDEA's Annasaheb Waghire College, Otur, Pune 412409 [3]P. G. and Research Centre, Yashavantrao Chavhan Institute of Science, Satara, 415 001- India.
Email kgkanade@yahoo.co.in | +91- 9881711038 Tel. : (91)-02162-234392

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ABSTRACT

The comparative study of surface activation of MgO under thermal and microwave heating was performed for Wittig reaction under grindstone technique. The nanocrystalline MgO obtained by thermal decomposition of alkali leached $Mg(OH)_2$ under hydrothermal condition and characterized by XRD, UV, IR and Hammett indicator method. Nanocrystalline MgO is activated under thermal and microwave heating for different scale of time and surface activated MgO used as solid base in Wittig reaction. Surface basicity's are compared for both techniques. Activation of surface is studies by IR techniques and phenolphthalein Hammett indicator method. All results viz. Surface basic activity, IR techniques and Hammett indicator methods suggested that thermal activation of MgO is superior over microwave activation.

Key Words: Surface Activation, Thermal Heating, Microwave Heating, Wittig Reaction.

INTRODUCTION

Surface activation of heterogeneous catalyst is an important task in order to carry out chemical reactions in an economic way according to Pushpaletha et al [1]. The reactivity of catalysts depends on activity of surface. For this purpose, different physical and chemical methods have been developed for activation of catalysts.

Hideshi [2] reported alkaline earth metal oxides are activated by conventional thermal treatments while Xinhuan et al [3] reported that transition metal is activated by microwave, sonochemical and irradiation techniques. Bio-activation methods are also used for some metal oxide activation. Zeolites are activated by acid treatments as reported by Xie [4]. Magnesium oxide is a solid base in different organic reactions such as Aldol condensation, Clainsen-Schimdt Condensation, Knoenvengal condensation, Coupling reactions, Wittig reaction, double bond isomerization etc [5-7]. Wittig reaction is base assisted reaction of phosponium salt with aldehyde or ketones through phosphorus ylides formation. It is known for selective synthesis of trans-alkene, important in perfumes, pharmaceutical drugs and vitamins as reviewed by Horst Pommer [8]. This reaction can proceed in presence of heterogeneous solid base MgO. MgO is required for generation of phosphorus ylide from phosponium salt by abstraction of acidic proton. This heterogeneous surface basic nature of MgO makes it a superior solid base. MgO exhibit surface basic activity due to its surface low coordinated oxygen's as reported by Ferretti and et al [9]. Low coordinated oxygen's such as 5 coordinated, 4 coordinated and 3 coordinated oxygen's are present on surface, terrace and corners on crystal lattice. Corma and Iborra [10] observed that 3 coordinated oxygen's are more basic over 4 and 5 coordinated oxygen. But these low coordinated basic sites of MgO is masked by chemisorption of CO_2 and water vapors at ordinary temperature. CO_2 and water responsible for carbonation and hydroxylation of magnesium oxide surface and hence basic activity of surface is destroyed. Tanabe and Yamaguch [11] showed that at very high temperature CO_2 and water are eliminated for preservation of surface basic activity. For this purpose, MgO solid base is activated at very high temperature prior to use in catalytic applications. High energy consumption by conventional thermal heating limits use of MgO in catalytic applications.

Microwaves are electromagnetic radiations ranging from 300 MHz to 300 GHz wavelength suggesting its less energetic nature. However, Raghubar [12] reported that microwaves are responsible for heating materials through dielectric polarization, dipolar polarization and conduction effect. Industrially, microwave heating is employed for ore grinding, pretreatment of gold, reduction of metal oxides, drying and anhydration, leaching of minerals and waste management [13-18]. Such multipurpose applicability of microwave heating required its use in catalytic applications too [19]. Many reports suggest microwave can be successfully used for activation of catalysts for chemical reactions. With this view, proposed research work uses microwave heating for surface activation nanocrystalline MgO as a solid base catalyst in Wittig reaction and results are compared with conventional thermal activation.

METHODOLOGY

Commercial MgO, NaOH flakes, benzaldehyde, ethyl bromoacetate triphenyl phospine, phenolphthalein benzoic acid and organic solvents were purchased from Loba Chemicals and used without further purification. The nanocrystalline MgO catalysts are characterized by XRD, FESEM, UV-DRS, FT-IR techniques. X-ray diffraction (XRD) analysis of the synthesized material was carried out using Bruker AXS model D-8, (10 to 80^o range, scan rate $=1^o$ min^{-1}) equipped with a monochromatic and Ni-filtered Cu Kα radiation. SEM analysis was used to determine particle morphology of the desired powder catalysts using HITACHI S-4800 model. The UV-DRS spectra are determined using Shimadzu UV-3600 instrument. For characterization of Wittig reaction product ethyl cinnamate, HR-MS is taken on Bruker Compass Data Analysis 4.2. ^{1}H-NMR analysis of products was carried out using Bruker model.

Preparation of nanocrystalline MgO: For preparation of nanocrystalline MgO, 5 g commercial MgO powder is added with stirring to 100 ml 10 M NaOH in 200 ml capacity teflon reactor with stainless still outer jacket. It is subjected for alkali leached hydrothermal reaction at 180 ^{O}C for 24 hrs. After cooling, the reaction content is transferred to 500 ml water in a beaker. It is diluted and washed with 20 liter deionized water and excess alkali is neutralized with very dilute HCl. This content is filtered on suction pump using whatmann filter paper no 41 and dried at 60^O C for 6 hrs. The resulting magnesium hydroxide is calcined at 450 ^{O}C according to procedure of Ding and et al [20] to obtain nanocrystalline MgO catalyst.

Activation of nanocrystalline MgO under thermal heating: For measurement of catalytic activity of nanocrystalline MgO, it is activated thermally at 700 0C in a muffle furnace for different scale of time in minutes and immediately used in Wittig reaction under grindstone techniques.

Activation of nanocrystalline MgO under Microwave heating: For measurement of catalytic activity of nanocrystalline MgO, it is heated in commercial microwave oven at 500 Watt for different scale of time in minutes and immediately used in Wittig reaction under grindstone technique.

Preparation of phosponium salt from ethyl bromoacetate and triphenyl phospine: Ethyl bromoacete and triphenyl phspine are stirred in toluene solvent in one neck R. B overnight. The resulting product was filtered over Buchner funnel on vacuum pump and washed with excess of toluene solvent. The product was vacuum dried.

Measurement of catalytic activity of nanocrystalline MgO in Wittig reaction: (6.7 mmoles) benzaldehyde, (4.7 mmoles) phosponium salt are crushed with 0.100g activated MgO in a mortar using pestle for about one hour. Initially reaction mixture liquefies but after this it solidified indicating the completion of reaction. Reaction is monitered by TLC. After this DMF solvent is added in reaction mixture and catalysts is separated by centrifugal separation at 5000 rpm. Reaction mixture is subjected for work up with water and ethyl acetate to remove excess of DMF. Products olefin and triphenyl phospine oxide are purified and separated on silica loaded column using pure hexane as eluent. The product of Wittig reaction is characterized by HR-MS, ^{1}H-NMR techniques.

RESULTS AND DISCUSSION

Preparation of nanocrystalline MgO is carried out using alkali leached hydrothermal method as given in experimental section. It is activated under both conventional heating as well as microwave heating. As synthesized product materials were characterized by using XRD, UV-DRS, FT-IR and Hammett indicator method.

XRD Analysis of nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO:

Figure 1 shows the XRD patterns of nanocrystalline magnesium hydroxide (**fig. 1a**) and nanocrystalline MgO (**fig. 1b**). The XRD analysis of nanocrystalline MgO shows the XRD peaks are matching with $Mg(OH)_2$ the corresponding 2θ values at 18.52, 32.89, 37.99, 50.86, 58.63, 62.05, 68.32 and 72.04 degrees which corresponds to 001, 100, 101, 102, 110, 111, 103, 201 planes respectively. This 2θ values with corresponding planes indicates the hexagonal crystal system with brucite phase (JCPDS file no 44-1482). As synthesized $Mg(OH)_2$ is further calcined at 450 ^{O}C. At 450 ^{O}C the hexagonal $Mg(OH)_2$ is completely converted to cubic MgO **(Fig. 1b).** The corresponding 2θ values of XRD patterns at 36.91, 42.88, 62.29, 74.68, and 78.61 with planes 111, 200, 220, 311, 222 respectively are well matched with cubic phase of MgO (JCPDS file no 45-0946).

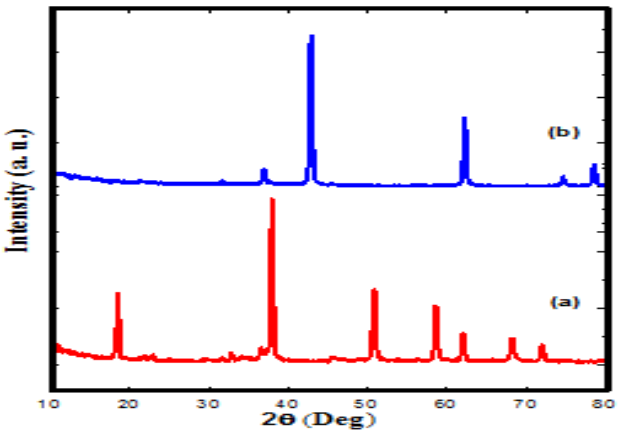

Figure 1. XRD Analysis of nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO

UV-DRS Analysis of nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO.:

Figure 4 shows the UV diffused absorption spectra of nanocrystalline $Mg(OH)_2$ (**fig. 2a**) and nanocrystalline MgO (**fig. 2b**) shows formation of pure phase. For nanocrystalline $Mg(OH)_2$ shows absorption band at 271 nm with red shift at 347 nm as observed by [21]. The sharp absorption band at 271 nm confirms the presence of Mg^{+2} ion. These multiple sharp absorption band of UV-DRS analysis is an important tool for gaining the idea about surface basicity of MgO. In case of nanocrystalline MgO absorption band at 230 nm and 280 nm are responsible for presence of 4 coordinated and 3 coordinated surface oxygen's [2]. In

case nanocrystalline MgO, the absorption band at 281 nm with red shift at 369 nm suggests the presence of only 3 coordinated surface oxygen's. The band at 230 nm is not appeared confirming the absence of 4 coordinated oxygen's on surface. This indicate the hydrothermal alkali leached methodology is useful enhance the more reactive 3 coordinated on surface of MgO.

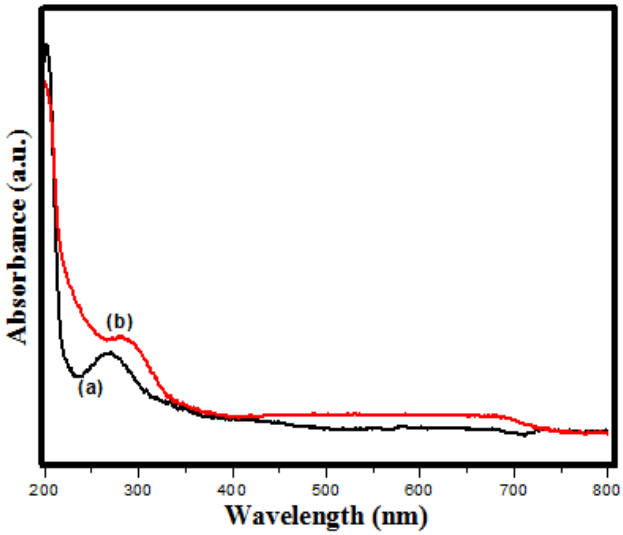

Figure 2. UV-DRS Analysis of (a) nanocrystalline $Mg(OH)_2$ and (b) nanocrystalline MgO

FT-IR Analysis of nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO.:

Figure 5 shows the FT-IR spectrums nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO. Two main regions in range of 400-850 cm^{-1} are observed in FT-IR spectrum. In first region, the bands due to different fundamental Mg-O vibrations are observed between 400-500 cm^{-1} as observed by Raman [23] In second region combination bands of fundamental vibrations appeared between 550-850 cm^{-1} [24]. Different types of IR bands in this two regions suggests the Mg-O vibrations and also.

Two bands appeared at between 1400-1500 cm^{-1} indicates the adsorption of CO_2 on MgO surface which is also supported with a band near small band at 2300 cm^{-1}[25]. The sharp peak at 3693 cm^{-1} indicates the O-H stretching vibrations in $Mg(OH)_2$. No significant bands are appeared between 3400-3600 cm^{-1} for nanocrystalline MgO confirms the calcination of $Mg(OH)_2$ to cubic MgO.

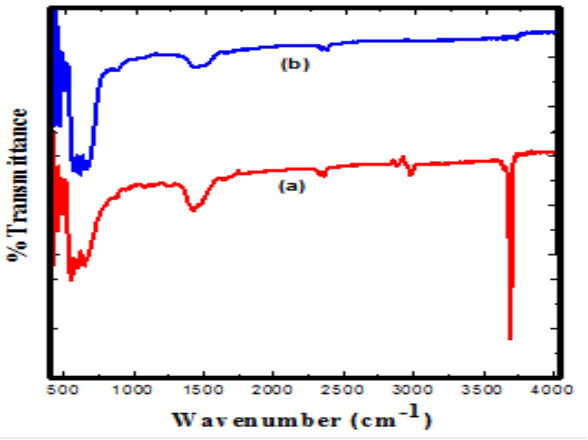

Figure 3. FT-IR Analysis of (a)nanocrystalline $Mg(OH)_2$ and (b)nanocrystalline MgO

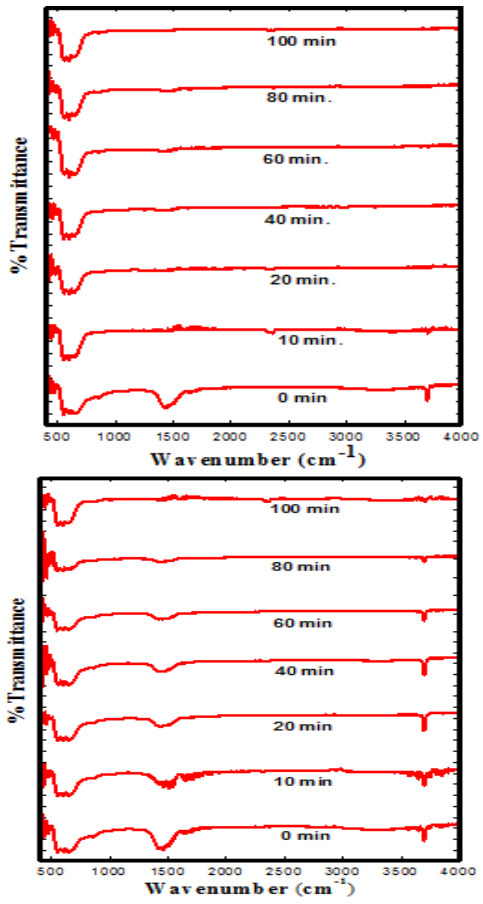

Figure 4. FT-IR Analysis for (a) Thermal activation and (b) Microwave activation of nano. MgO for different scale of time

FT-IR studies gives clue about the surface and corner oxygen which adsorb CO_2 and water vapors at ordinary temperature. Very high temperature is required for elimination of CO_2 and water vapors hence for surface activation. For this purpose, nanocrystalline MgO is activated under thermal

heating at 700 ^{0}C (**fig. 3a**) and microwave heating at 500 watts (**fig. 3b**) for different scales of time for 0, 10, 20, 40, 60 80 and 100 minutes for surface activation. IR spectra for each time are compared for surface carbonates and hydroxyl groups for both heating approaches. For thermally activated nanocrystalline MgO, the IR absorption peak at 1400-1600 cm^{-1} and 3600 cm^{-1} for carbonates and hydroxyls respectively are completely vanishing confirming activation of surface within 20 minutes. But for microwave activated nanocrystalline MgO, even after 100 min heating, persistence of carbonates and hydroxyls peaks confirming the MgO surface is still covered with CO_2 and water vapors. Careful observation of microwave heated FT-IR spectra for carbonate and hydroxyl peaks shows that MgO is not good microwave absorber as observed by Aguilar and Pearce [26] by thermocouple study. FT-IR study shows that thermal activation method is superior over the microwave activation method.

FESEM Analysis of nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO:

Figure 5 shows FE-SEM photographs of nanocrystalline $Mg(OH)_2$ and nanocrystalline MgO. The FESEM photograph of Nano sized $Mg(OH)_2$ shows formation of nano sheets with 20 nm thickness under alkali leached hydrothermal condition. This nano sheets during the calcination of $Mg(OH)_2$ breaks down into nano sized MgO hexagonal sheets with same thickness. This hexagonal plates are stacked on above each other. FESEM photographs shows, at nano size large number of low coordinated oxygen's on surface of MgO increases. MgO at nano size exhibit maximum basic catalytic activity.

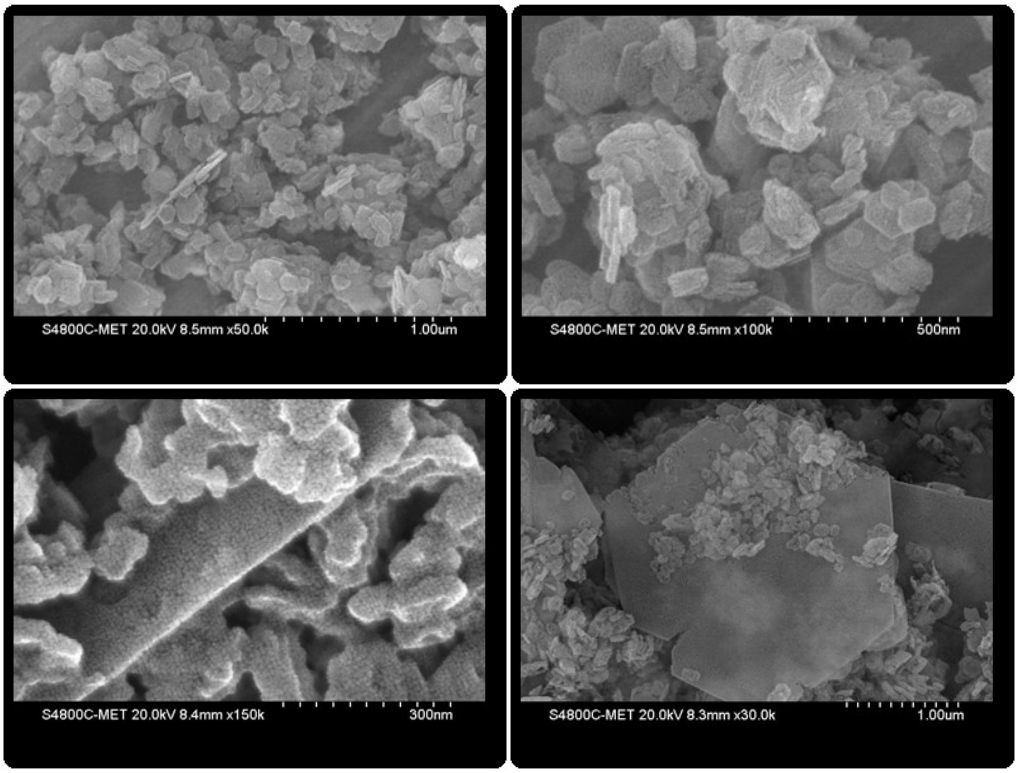

Figure 5. FESEM-Photographs of (a-b) nanocrystalline Mg(OH)2 and (c-d) nanocrystalline MgO

Scheme 1. Wittig reaction of benzaldehyde with phosponium salt in presence of nanocrystalline MgO using Grindstone technique.

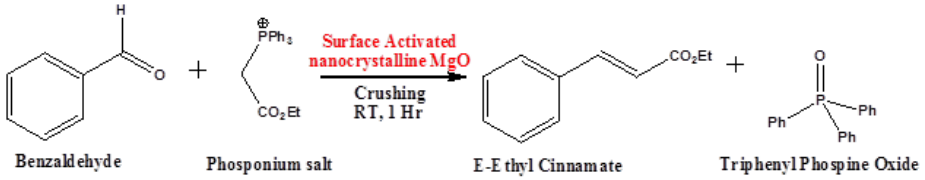

Table 1. Effect of thermal and microwave activation on catalytic activity of nanocrystalline MgO In Wittig reaction

No	Time of Heating/Min	Surface basicity/ mmoles/g	
		Thermal heating (700 ^{O}C) (a)	Microwave heating (500 W) (b)
1	0	40	40
2	10	50	45
3	20	52	48
4	40	65	50
5	60	72	55
6	80	80	62
7	100	92	65

Reaction condition: 6.9 mmoles benzaldehyde and 4.6 mmoles phosponium salt crushed with 0.100 g nanocrystalline MgO for 1 hr at RT.

Table 2. Effect of thermal and microwave activation on surface basicity's of nanocrystalline MgO in Wittig reaction.

No	Time of Heating/Min	Surface basicity/ mmoles/g	
		Thermal heating (700 ^{O}C) (a)	Microwave heating (500 W) (b)
1	0	0.02	0.02
2	10	0.1	0.08
3	20	0.25	0.16
4	40	0.38	0.22
5	60	0.55	0.30
6	80	0.70	0.40
7	100	0.85	0.48

Titration condition: 0.100 g nanocrystalline MgO is suspended in non-polar 10 ml benzene solvent, 1 ml phenolphthalein indicator allowed to adsorb over its surface and titrated with 0.1 N benzoic acid.

Measurement of catalytic activity of thermal and microwave activated nanocrystalline MgO:

With a specific amount of activated nanocrystalline MgO (0.100 g) catalysts 6.9 moles benzaldehyde and 4.76 moles phosponium salt are crushed in mortar and pestle for 1 hr. After workup and purification, Wittig product ethyl cinnamate is characterized by HR-MS and ^{1}H-NMR. Basic catalytic activities are compared for thermal and microwave activation method.

Measurement of surface basicity of nanocrystalline MgO for thermal and microwave heating.

As observed from table 1. Catalytic activity of nanocrystalline MgO differs under thermal and microwave activation methods in Wittig reaction. Under thermal activation methods catalyst is activated within only 20 min so it shows 50 % catalytic activity for 20 min (**Table 1, entry 3a**) and 92 % (**Table 1, entry 7a**) for 100 min also catalytic activity regularly goes on increasing. Under microwave irradiation even after 100 min, catalyst is not activated indicating 45 % to 65 % catalytic activity within 20 to 100 min heating period. Catalytic activity of nanocrystalline MgO shows same trends as observed in FT-IR study. This shows that under microwave heating, MgO shows poor catalytic activity.

Hammett indicator method is used for determination of surface basicity of heterogeneous solid bases [27]. So this method is employed for surface basicity determination of nanocrystalline MgO for both approaches. The phenolphthalein dye is adsorbed over MgO surface and after adsorption solution shows pink color. It is titrated with benzoic acid. So amount of benzoic acid required in ml is measure of surface basicity of nanocrystalline MgO in mmoles/g.

Table 2. represents the surface basicity's of nanocrystalline MgO activated under thermal and microwave heating. From observation's, it is clear that, surface basicity of nanocrystalline MgO is a function of activation temperature and condition. In thermal heating, change from 0.02 mmoles/g to 0.85 mole observed from 0 min to 100 min so there is approximately 50-fold increase in basicity observed while under microwave activation surface basicity changes from 0.02 to 0.48 mmoles/g from 0 to 100 min suggesting for only 25-fold increase. Poor basicity of nanocrystalline MgO under microwave heating is attributed to coverage of surface active basic sites by CO_2 and water vapors, and very high temperature is required for removal of these. Thermally MgO can be effectively heated for activation while under microwave, due to inability of MgO to absorb heat, it is not activated even up to 100 min.

Thus, FT-IR techniques, catalytic activity in Wittig reaction and Hammett surface basicity measurement was employed in order to compare surface activation of nanocrystalline MgO under thermal and micro-

wave activation. Our techniques for comparisons are easy and useful in order to scaling up the organic reactions assisted by solid bases.

CONCLUSION

Pure nanocrystalline cubic MgO prepared by calcination of hydrothermally prepared nanocrystalline $Mg(OH)_2$. Nanocrystalline MgO is activated under thermal and microwave heating for different scale of time. FT-IR study for different time in min suggests that nanocrystalline MgO can be easily activated under thermal condition rather than microwave. Catalytic activity study in Wittig reaction indicates that thermally activated MgO is more basic over microwave activated and surface basicity measurement by Hammett indicator method shows that under thermal heating nanocrystalline MgO can be quickly activated than microwave heating.
In nutshell, thermal activation of nanocrystalline MgO is superior over microwave activation for catalytic applications.

Analysis of Wittig product: E- Ethyl cinnamate
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).

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