

Comparison of Sol Gel and Dehydration Magnesium Oxide (MgO) as a Catalyst in Michael Addition Reaction

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Abstract: Magnesium oxide (MgO) was prepared by dehydration of magnesium carbonate method and sol gel method. The prepared MgO powders were calcined at the temperature of 200, 400, 600, and 800 °C for two hours. Then, the samples were characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM). In order to investigate the prepared MgO, the samples were applied in Michael addition reaction to produce diethyl 2-(3-oxo-1,3-diphenylpropyl) malonate. The highest percentage yield of 94% was obtained from MgO prepared from sol gel method and calcined at 800 °C.

Keywords: Magnesium oxide, sol gel MgO, Michael addition reaction

1. Introduction

One of the most versatile metal oxides known is magnesium oxide (MgO) which has various importance applications in industrial. For example, it has been used widely in catalysis, ceramics, color pigments, electronics, coating technology, toxic waste remediation, and antibacterial materials [1]. The studies of synthesis, characterization, and reactivity of the preparation of MgO can be obtained by various methods to enhance the properties and morphologies of the materials [2]. Conventionally, sol gel, thermal decomposition, dehydration and hydrolysis methods are mostly used to synthesize MgO due to the simple methods, cost effectiveness, and capable of producing other unique properties [3]. Producing MgO with large crystallite size and low surface area-to-volume ratio is the drawback with this method that limits its applications for nanotechnology [3]. There are methods which are quite sophisticated by expense or apparatus, which are the wet impregnation, glycine-nitrate combustion, flame metal combustion, and chemical precipitation [4].

Important factors affected the catalytic properties of sol gel MgO are crystallite size, surface area, structural defects and acid base concentration are [5]. There are various reactions that has been devoted to the use of solid base catalysts obtained fine chemicals, pharmaceuticals, and valuable compounds. In the field of fine chemical production, MgO has been studied for the large complex molecule include carbon-carbon bond forming reactions such as Michael additions or Knoevenagel condensations. In particular, the study of Michael addition reaction involve the addition of active methylene compounds, alcohol, thiols, to α,β -unsaturated carbonyl compounds as to construct carbon-carbon bonds which the mechanism involved the formation of anion and protonation product [6].

In this study, MgO samples were prepared by using two methods and the prepared samples were compared with commercial MgO in both characterization and application processes. The primary objective of this paper is to study the effect of commercial and prepared MgO applies as a catalyst in Michael addition reaction.

2. Experimental

2.1 Materials

The chemicals and reagents used were purchased from standard commercial suppliers R and M chemicals and used as received without further purification. Magnesium carbonate, magnesium ethoxide, concentrated hydrochloric acid (conc. HCl), concentrated ammonium hydroxide (conc. $\text{NH}_4(\text{OH})$), chalcone, diethyl malonate, ethanol, toluene, and distilled water were the main materials that have been used in the whole study.

2.2 Preparation of magnesium oxide (MgO)

This study aimed for producing MgO powder by using different methods to compare the effect on MgO applied in the Michael addition reaction. Thus, the dehydration of magnesium carbonate and sol gel method were the two main methods used to prepare MgO powder. In this study, the prepared magnesium oxide (MgO) using dehydration magnesium carbonate method was labeled as MgO-D and using sol gel method was labeled as MgO-SG.

2.2.1 Dehydration of Magnesium Carbonate

Firstly, magnesium carbonate, $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ was added and suspended in 750 mL of distilled water. The solution was stirred at temperature around 80 for 30 minutes. The suspended $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ was filtered using Buchner funnel and dried at temperature of 90 °C for 24 hours. Calcination has been done at various

temperature of 200, 400, 600, and 800 °C for 2 hours to obtain dehydrated $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$ and labeled MgO-D 200, MgO-D 400, MgO-D 600, and MgO-D 800 respectively. The powder obtained was transferred to sealed vials and placed in a desiccator.

2.2.2 Sol Gel Method MgO (MgO-SG)

As for sol gel method, magnesium ethoxide has been refluxed in a mixture of ethanol, water, and concentrated HCl. Once the ethoxide was completely dissolved, concentrated NH_4OH was added till pH 9. After 40 hours of continuously refluxed, milky yellow gel has been formed. The milky gel solution undergoes centrifugation to separate the gel. The gel has been calcined at various temperatures of 200, 400, 600, and 800 °C for 2 hours and labelled MgO-SG 200, MgO-SG 400, MgO-SG 600, and MgO-SG 800 respectively. The powder obtained was kept in sealed vials inside a desiccator.

2.3 Characterization and Application

The prepared MgO samples were characterized using fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM). The solution synthesized by the Michael Addition reaction had been analyzed by using gas chromatography equipped with flame ionization detector called GC-FID (Shimadzu GC 2010 Plus)

3. Results and Discussion

The characterizations of the commercial and prepared MgO were performed by using fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM).

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.1 shows FTIR spectrum form commercial MgO. From the spectrum, O-H stretching vibration of adsorbed water molecule was observed at frequency 3435 cm^{-1} [7]. The absorption at 1437 cm^{-1} assigned to Mg-H that indicate to the formation of hydride ion. The deformation vibration of Mg-O-Mg was observed at 423 and 675 cm^{-1} respectively. FTIR spectrum data of the commercial MgO are listed in Table 3.1.

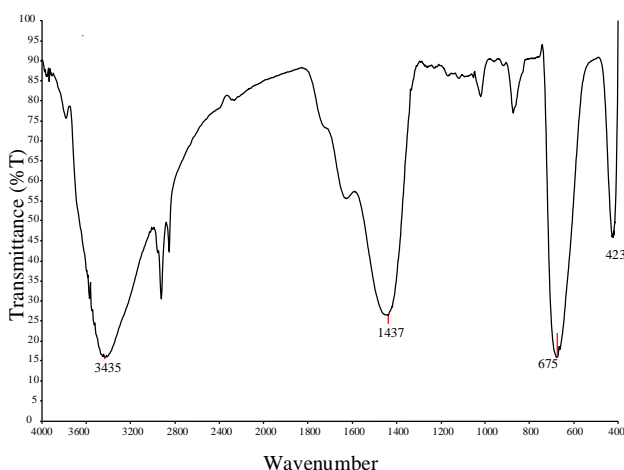


Figure 3.1 FTIR spectrum of commercial MgO

Table 3.1 FTIR spectral data of the commercial MgO

Frequency (cm^{-1})	Peak assignment
3435	O-H stretching vibration of adsorbed water molecule
1437	Formation of Mg-H
423 and 675	Deformation vibration of Mg-O-Mg

FTIR spectra of MgO that was prepared by using dehydration of magnesium carbonate method are represented in Figure 3.2. The sharp peak absorption was observed at 3698 cm^{-1} that indicated the presence of unassociated hydroxyl due to the chemisorption of water which fragments occurred by the heterolytic dissociation of the HO-H bond and subsequent attachment are generated at external sites of MgO lattice [8].

Broad peak absorption in the range of $3420\text{--}3460\text{ cm}^{-1}$ was assigned to O-H stretching vibration of adsorbed water molecule which indicates the physisorption of water. The formation Mg-H was observed at broad peak absorptions at $1420\text{--}1460\text{ cm}^{-1}$ due to different peripheral Mg^{2+} sites. The deformation vibration of Mg-O-Mg was observed at $450\text{--}680\text{ cm}^{-1}$. The sharp peak at range 3700 cm^{-1} increases as the temperature increase. Overall, the results showed the peak decreases due to the high calcination temperature gives better elimination of water molecule on the surface of sample.

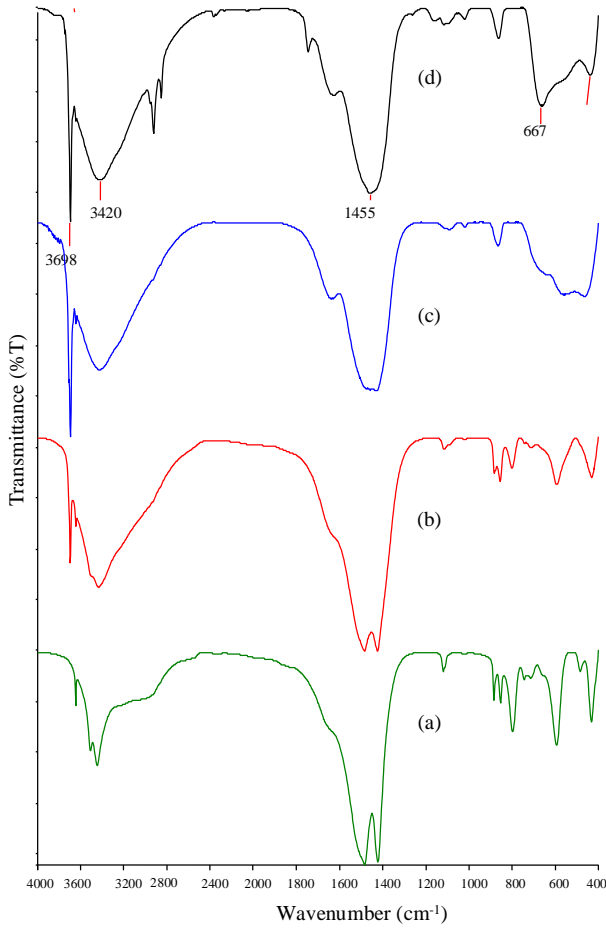


Figure 3.2 FTIR spectra of MgO obtained by dehydration of magnesium carbonate at different calcination temperature; (a) MgO-D at 200, (b) MgO-D at 400, (c) MgO-D at 600 and (d) MgO-D at 800 °C.

While Figure 3.3 shows the FTIR spectrum for the MgO that was prepared using sol gel method. Similar results to dehydration samples were obtained where broad peak around 3422 cm⁻¹ was observed which indicated physisorption of water. Both samples show the presence of the impurities from KBr at 1458 cm⁻¹. The wavenumber at 543 cm⁻¹ refer to the deformation of Mg-O-Mg. An unassociated hydroxyl based on chemisorption of water peak was observed at 3699 cm⁻¹. This peak disappeared at the higher temperature proven the conversion of Mg(OH)₂ to MgO during calcination was considered as almost complete.

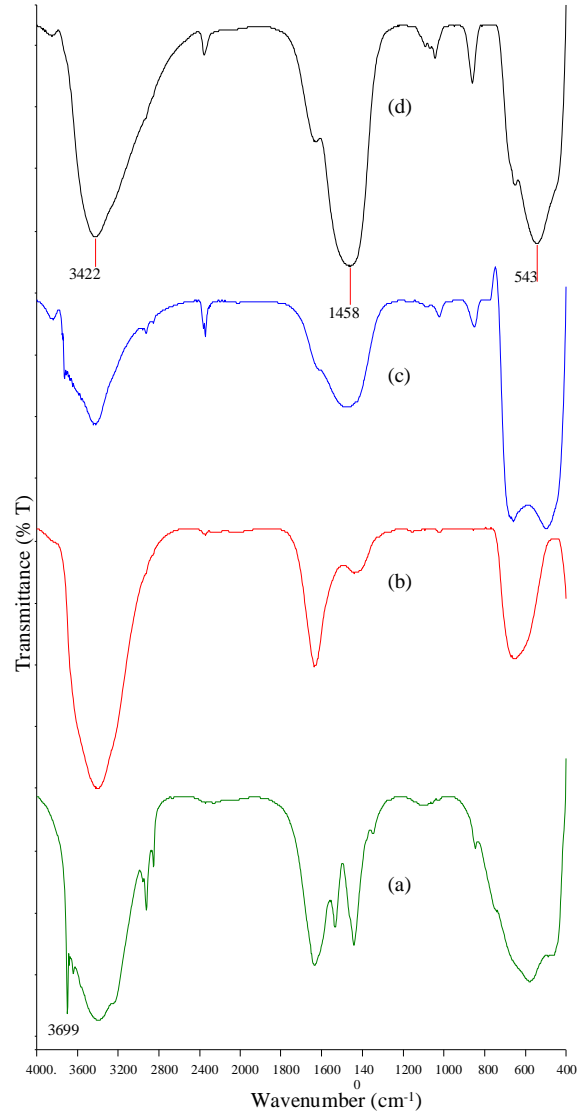


Figure 3.3 FTIR spectra of MgO prepared by sol gel method at different calcination temperature; (a) MgO-SG at 200, (b) MgO-SG at 400 (c) MgO-SG at 600 and (d) MgO-SG at 800 °C.

3.2 X-ray Diffraction Spectroscopy (XRD) Analysis

The commercial MgO was characterized using X-ray diffraction to study its phase analysis, pattern, and crystalline structure analysis by X-ray diffraction. Figure 3.4 shows the XRD analysis for the commercial MgO powder with three clear and sharp peaks. Referring to JCPDS file for MgO, this pattern shows a periclase MgO (cubic) that indicates the highly crystalline structure of MgO [9]. The corresponding values are represented in Table 3.2 the peak assignment of the commercial MgO.

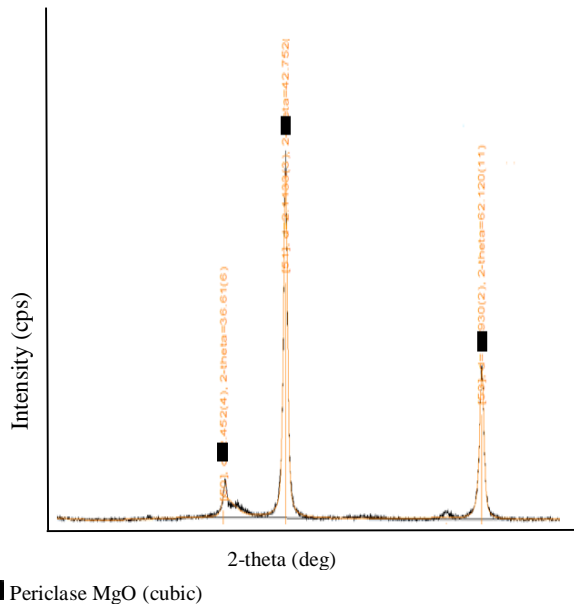


Figure 3.4 XRD diffractogram of the commercial MgO

The XRD data for prepared MgO by dehydration of magnesium carbonate method that calcined at 200, 400, 600, and 800 °C can be seen at figure 3.5. Through the XRD pattern, the diffraction peak was discovered in crystal structure of MgO at 2.432, 2.1056, and 1.4891 Å which referred to the JCPDS database and exhibit a periclase MgO (cubic). The brucite Mg(OH)₂ (hexagonal) was observed at 2.725, 2.365, 1.794, and 1.57 Å respectively.

MgO-D 200 and MgO-D 400 showed an amorphous phase of MgO and contained more brucite Mg(OH)₂ (hexagonal) compared to MgO-D 600 and MgO-D 800. The periclase MgO (cubic) obtained by calcination at 800 °C was exactly proven that the prepared MgO-D 800 shows crystalline structure with a presence of one peak brucite Mg(OH)₂ (hexagonal). This might be due to the fast interaction between the atmospheric moisture and the solid MgO [10].

The XRD pattern for overlay of the prepared MgO by sol gel method that is calcined at different temperature was show in figure 3.6. MgO-SG 400, MgO-SG 600, and MgO-SG 800 were obviously shown that indicate as periclase MgO (cubic) at each peaks obtained from the XRD patterns. The extraneous signals of brucite Mg(OH)₂ (hexagonal) was absence due to heat treatment that fully evaporated the moisture of water [11]. These similar periclase MgO (cubic) peaks were compared and MgO-SG 800 which shows the strongest crystalline phase.

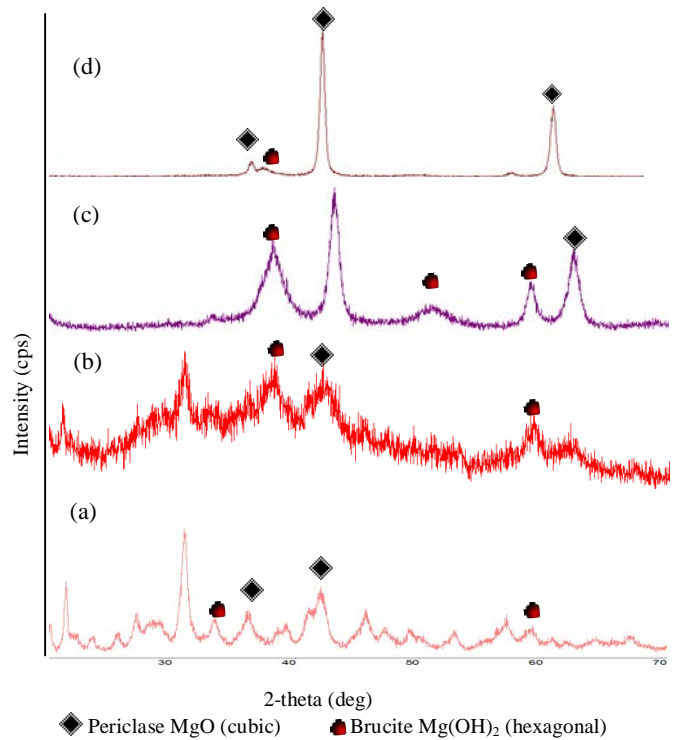


Figure 3.5 XRD diffractogram of the prepared MgO by dehydration of magnesium carbonate method at different calcinations temperature; (a) MgO-D at 200, (b) MgO-D at 400, (c) MgO-D at 600 and (d) MgO-D at 800 °C.

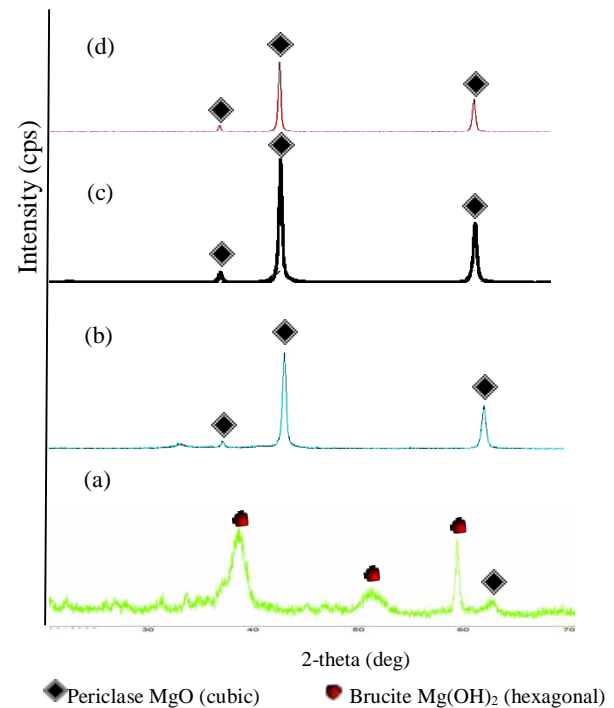


Figure 3.6 Peak assignments of the prepared MgO by sol gel method that calcined at different temperature were obtained in XRD patterns; (a) MgO-SG at 200, (b) MgO-SG at 400 (c) MgO-SG at 600 and (d) MgO-SG at 800 °C.

3.3 Scanning Electron Microscope (SEM) Analysis

Figure 3.7 shows the surface morphology of the commercial MgO with spherical like shape and narrow size distribution [12]. The image was obtained from backscattered electron SEM

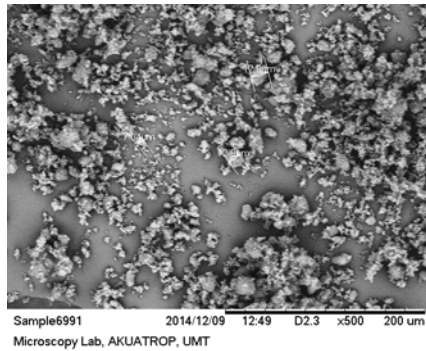


Figure 3.7 SEM micrograph of commercial MgO (MgO-CM) with magnification 500X.

Figure 3.8 shows the MgO samples that calcined at 200-800 °C which labeled as MgO-D 200, MgO-D 400, MgO-D 600, and MgO-D 800 respectively. The image from the SEM shows the size MgO-D 200 and MgO-D 400 seem a bit larger on its particle size (a-b) compared to MgO-D 600 (c) and MgO-D 800 (d) that was calcined at highest temperature showed smallest size distribution which has great tendency for agglomeration to occur caused by their surface energy could lead to the formation of high surface area and crystallinity [13].

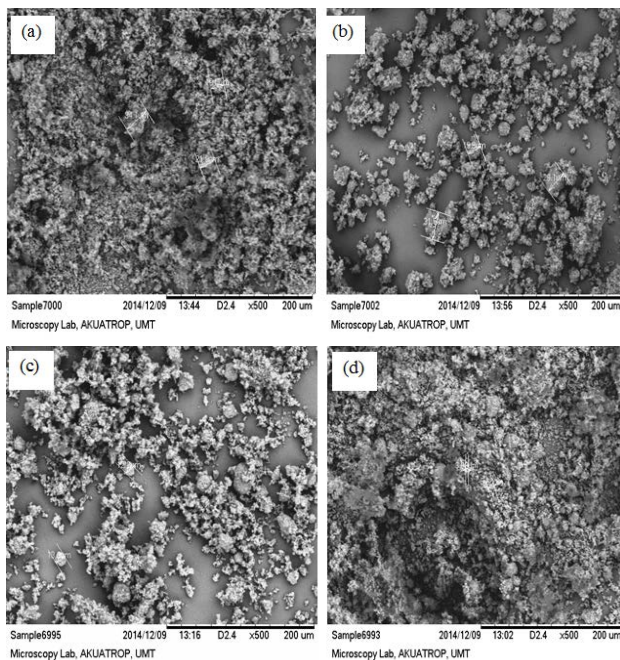


Figure 3.8 SEM micrographs of prepared MgO by dehydration of magnesium carbonate with magnification 500X: (a) MgO-D 200 (b) MgO-D 400 (c) MgO-D 600 (d) MgO-D 800

While Figure 3.9 shows the SEM micrograph of MgO powder prepared by sol gel method which calcined at different temperature for two hours. The SEM image was characterized by SEM that has secondary and backscattered electron. It shows that the average particle size characterized by MgO-SG was smaller than MgO-D even though the magnification by both prepared MgO was similar (x500).

MgO-SG 200 (a) that consist of brucite $Mg(OH)_2$ (hexagonal) and amorphous structure shows a bit larger than the rest of prepared MgO due to the presence of water as the MgO is hygroscopic and calcined at lowest temperature [14]. The spherical-like shape and size distribution obtained in MgO-SG (b-d) showed quite similar and these observations were correlated when XRD pattern of periclase MgO (cubic) could be seen in XRD analysis.

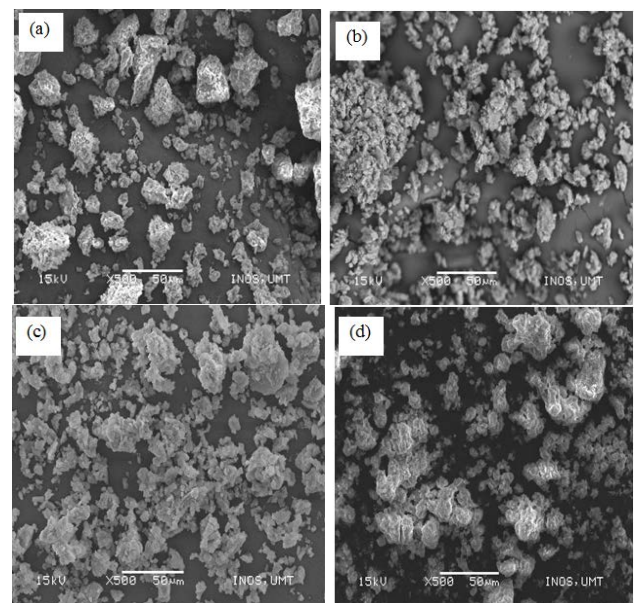


Figure 3.9 SEM micrographs of prepared MgO by sol gel method with magnification 500X: (a) MgO-SG 200 (b) MgO-SG 400 (c) MgO-SG 600 (d) MgO-SG 800

3.4 Synthesis of Michael Addition Reaction

3.4.1 GC-FID Analysis

The synthesis of Michael reaction had been analysed by gas chromatograph equipped with flame ionization detector (GC-FID) in which the parameter was followed as represented in Table 3.2. The column used was BPX5 column and it was compatible with this reaction that yields the aromatic hydrocarbon which features to be a non-polar and the column itself as an ideal for over 80 % routine GC analysis. Figure 3.10 shows the asymmetric Michael addition reaction of diethyl malonate as Michael donor to α, β -unsaturated ketone.

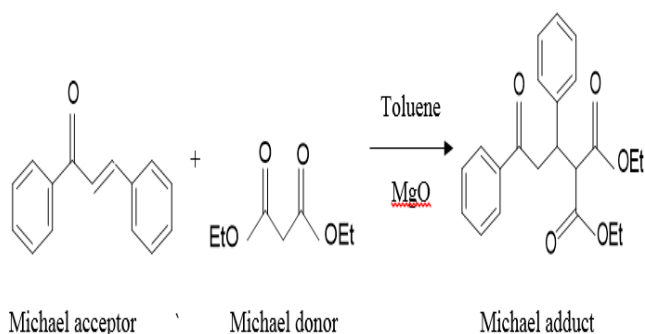


Figure 3.10 Schematic diagram of Michael addition reaction of diethyl malonate as Michael donor to chalcone as Michael acceptor to yield diethyl 2-(3-oxo-1,3-diphenylpropyl) malonate as Michael adduct

Table 3.2 Parameter of GC-FID analysis of Michael addition reaction of diethyl 2-(3-oxo-1,3-diphenylpropyl) malonate

GC Parameter	Value
Injection port temperature	320 °C
Injection oven temperature	50 °C
Oven temperature program	50 °C to 300 °C at 15 °C/min Hold at 300 °C for 10 minutes
Helium, flow rates	Split ratio : 5:1 Purge flow : 3.0 L/min Column flow : 0.80 mL/min Make up (FID) : 30.0 mL/min
Compressed air (FID)	400 mL/min
Hydrogen (FID)	40.0 mL.min

Figure 3.11 show the Michael addition reaction that was analyzed in the absence of commercial MgO and the analysis shows the retention time of 4.859, 8.179, 16.851, and 19.505 minutes with respect to the peak represented of toluene, diethyl malonate, chalcone, and diethyl 2-(3-oxo-1,3-diphenylpropyl) malonate.

The Michael reaction with commercial MgO catalyst resulted higher percentage yield which is 72 % compared to the reaction without catalyst. Table 3.3 shows the overall percentage yield for Michael addition reactions under the optimized reaction conditions based on GC-FID parameters. The result for the prepared MgO from dehydration of magnesium carbonate shows that the calcined sample of MgO at 800 °C gave lower yield compared to the calcined sample at 600 °C. The prepared MgO that was calcined at 600 °C still gave high yield as this proved the yield of the synthesized MgO is much higher with the presence of MgO than without MgO catalyst.

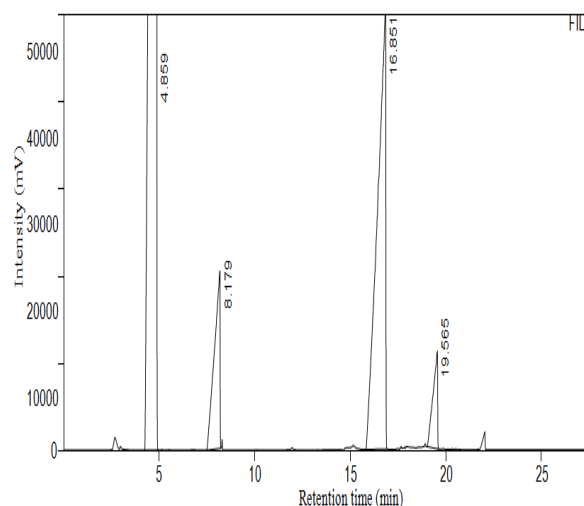


Figure 3.11 Chromatogram of Michael addition reaction that was carried out in the absence of MgO catalyst

Table 3.3 Optimization of the reaction conditions of Michael addition reaction^a

Entry	Classification	MgO catalyst	Description	Yield ^b (%)
1	Set A	Absence	Without MgO	56
2	Set B	Presence	MgO-CM	72
3	Set C	Presence	MgO-D 800	51
4	Set D	Presence	MgO-D 600	90
5	Set E	Presence	MgO-SG 800	94
6	Set F	Presence	MgO-SG 600	75

^a Reaction condition: DEM/chalcone/toluene/MgO = 4mmol/ 4mmol/ 4mL/ 0.4g, 2h

^b Determined on GC-FID using BPX5 column (29.5 m x 0.25 mm ID x 0.25 µm film)

In the presence of the prepared MgO catalyst prepared by sol gel method, the result showed highest yield obtained when used the samples calcined at 800 °C as a catalyst in the Michael reaction with 94%. While, the sample calcined at 600 °C gave 75%. Thus, the calcination temperature may affect the catalytic activity consist of number of active basic sites and its strength and the modification of synthesis MgO catalyst itself gave impact and enhanced the properties of MgO to yield better performance as a catalyst in reaction specifically organic reaction.

4. Summary

Both methods show that the best sample of MgO obtained were discovered to be the samples that were calcined at 600 °C and 800 °C. In Michael addition reaction, both prepared MgO was applied to investigate

the catalytic activity of MgO catalyst. The study showed absence of MgO catalyst in Michael addition reaction affect the result. The percentage yield obtained from MgO prepared from sol gel method and calcined at 800 °C which is 94 %. It can be concluded that even though the commercial MgO is easily obtained, the further investigating the MgO properties, the modification of MgO is required and necessary to enhance the catalytic activity when applied in any organic reaction.

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