Synthesis and characterization of MgO nanoparticle via microwave and sol-gel methods

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Abstract. This investigation aims to study the characterization of MgO nanoparticles prepared using two different routes via microwave method and sol-gel route. The characteristics of the fabricated of MgO nanoparticles were examined by FESEM, XRD, FTIR and BET. The results of XRD for microwave method and sol-gel route revealed peaks indicating the uniform crystalline. The images of FESEM of MgO nanoparticles by microwave method evinced an irregular shape, but the MgO nanoparticles synthesized by sol-gel route were found crystallites, nano spherical shape. The results of this work manifested that the MgO nanoparticles prepared via sol-gel route had smaller grain size as (≈ 50 nm) compared to the microwave method (≈ 72 nm). The specific surface area of the MgO nanoparticles using sol-gel route was more than with microwave route. FTIR examination reveals that the presence of Mg-O in the sample.

Keywords: MgO nanoparticles, Microwave, Sol-gel, FESEM, BET, FTIR

1- Introduction
At the last decades, nanoscience has considered the case of an important science with fundamental prospects in all the main sciences, such as chemical, physical, biological and engineering fields. The emerging fields of nanoscience and nanotechnology are leading to the technological uprising in the world [1]. MgO nanoparticles have been used as a solid base additive of acetone, a support material for Au and Ru, and a catalyst for the isotopic exchange reaction of oxygen. Magnesium oxide is an important material among the oxides because of its unique chemical and physical applications. For example, MgO has a high melting temperature (2850°C) and boiling temperature (3600°C) and possesses an ionic composition with an insulator band gap about (7 eV). The band-gap for MgO nanoparticles was defined by optical absorption techniques [2, 3]. MgO has many applications such as the processing of toxic chemical waste, an antibacterial material, refractory materials, superconductors materials and used as additive in the heavy fuel oil. [4, 5].

Many methods are used to the synthesis of nanoparticles MgO involving the hydrothermal method, sol-gel method, laser vaporization, combustion aerosol synthesis and chemical vapor deposition (CVD). Microwave method is considered an important method because of its several features of being faster, simpler and higher efficient of energy [6]. The properties and morphology of MgO nano structure are extensively dependent on the mechanism and the conditions of synthesis route.
Therefore, the main characteristic of magnesium oxide is improved in nanostructure and nano size. There are many limitations observed in the previous methods, such as requirement of complex the equipment, need of many steps in processing, long time, dissipation of energy, and high cost. Recently, microwave route has been used to prepare the MgO nanoparticles because it is more important than the traditional methods. The mechanism of microwave method depends on the dielectric heating, at which the material absorbed the microwave energy. In this case, the energy is converted into thermal energy or kinetic energy depending on the dipoles mobility and the electrical field direction. The changing in the electrical field of microwave radiation will lead to rotate the molecules, and then "internal friction' will happen in polar medium, and in turn causes a direct and fast heating [7]. The sol-gel route is an important route for manufacturing MgO nanoparticles because of many reasons, such as producing the MgO nanoparticles with a high surface area and narrow size distribution, simple process, and gives high products [8].

In the current work, MgO nanoparticles have been prepared via two different routes (microwave route and sol-gel route) and compared between them.

2- Experimental Procedures

2.1 Microwave route

1.22 g of magnesium nitrate [Mg (NO₃)₂, 6 (H₂O)] was blended with a solution (consist of deionized water about 20 ml and Urea [CO(NH₂)₂]) and then powering into the silica crucible. Afterward, the solution was stirring for 0.5 hour in order to obtain a homogeneous solution and followed by heating in microwave oven (850 W, 2450 MHz) for 15 min. Firstly, the solution was boiled and followed by dehydration and then decomposed by gases. The solution was boiling till the point of spontaneous combustion and then vaporized to create a solid matter. The solid matter was washed carefully using Ethanol and then drying in vacuum oven at 75°C for 2 hr. In the present work, Urea was used as a fuel. Finally, the fine MgO nanoparticle was calcined at 500 °C for 2 h at a heating rate of 5 °C/min.

2.2 Sol-gel route

Magnesium oxide nanoparticles can be synthesized using sol-gel route, which is done by various stages, such as blending process, stirring process, filtration process, drying process and calcination process [9]. Magnesium Nitrate [Mg (NO₃)₂, 6 (H₂O)] of purity (GC) 99% merck and Sodium Hydroxide (NaOH) powder of Gehalt (acidimetric) 99% merck were used in the present work. In the chemical reaction, distilled water was used as a solvent, while Ethanol (99.9% purity, AR grade) was used as a washing reagent respectively. At the first, distilled water was added to a compound of Mg Nitrate (5.903 g, 0.2 M) and then stirring the solution by magnetic stirrer for 45 min to obtain (solution A). The second step is preparing (solution B) as the following: 1.60 g, (0.2 M) of NaOH was blended with distilled water (200 ml) and kept under magnetic stirrer for 45 min to obtain (solution B). Afterward, (200 ml) of (NaOH solution B) was added to (solution A) of magnesium Nitrate [Mg (NO₃)₂, 6 (H₂O)] drop-wise by using glass rod, and the mixture was left for 30 min ultrasonic stirring. After that, this mixture was stirring by magnetic stirrer for 2 hours. After the stirring process, the mixture was left to rest for (2h), and then precipitation process is done at a bottom of the beaker, and then the precipitation material was filtered and washed several times by using a distilled water (4 times) followed by washing in Ethanol (2 times) so as to obtain a final product. The obtained material was kept in a vacuum oven at 80°C for 4 hours to remove the moisture by drying process. Finally, the fine MgO nanoparticle was calcined at 400°C for 3 hours.

2.3 Characterization of MgO nanoparticles

FESEM (Field Emission Scanning Electronic Microscopy model SIGMA VP) was used to define the characteristic of surface morphology such as the particle shape and particle size of MgO nanoparticles. The specific surface areas of MgO nanoparticles were measured by BET method using (Quantachrome CHEMBET 3000) device. Prior to the analysis, the samples were degassed at 120 °C for 2 h under saturated vapour pressure (85.56 KPa) overnight by flowing an inert gas to remove any absorbent molecules. The XRD pattern of MgO was defined utilizing X-ray diffractometer model (PanalyticalX’pert) using CuKα radiation with wave length at λ= 1.5405 Å. The FTIR spectroscopy of MgO powder was defined by Michelson interference in spectrum analysis, to study the surface interactions the MgO nanopowder.
3- Results and Discussion

3.1 XRD analysis

Figure 1 and Figure 2. Show the XRD patterns of peaks for MgO nanoparticles synthesized by microwave method and sol-gel routes. Figure 1 shows the XRD patterns of peaks for Mg(OH)2 and MgO nanoparticles. The dried precipitates depicted the reflections corresponding to the Mg(OH)2 phase. XRD emphasized that at the calcination 500°C, Mg(OH)2 (Hexagonal crystal system) was completely converted to MgO (cubic crystal system). As shown in Figure 1, the observed diffraction peaks of Mg(OH)2 at 2θ = 18.58, 37.98, 50.81, 58.60, 62.04, 68.20, 71.996 degree are associated with (001), (011), (012), (110), (111), (103), and (201) planes, respectively. These planes are created at d-spacing about of 4.77, 2.36, 1.79, 1.57, 1.49, 1.37 and 1.31 Å, respectively, which can be constituted to a hexagonal phase Mg(OH)2 (ICSD code 079198). Furthermore, it showed the sharp peaks which mean good crystallinity. The structural phase of MgO nanoparticles revealed that the diffraction peaks at 2θ = 36.94, 42.92, 62.15, 78.64 degree are associated at (111), (200), (220) and (222) planes, respectively. These planes are obtained when the d-spacing about 2.43, 2.10, 1.48 and 1.21 Å respectively, which they can be constituted in a cubic phase of MgO according to (ICSD code 064929).

Figure 2 illustrates the XRD peaks for MgO nanoparticles synthesized by sol-gel route. These peaks at 2θ = 36.86, 42.82, 62.16, 74.51, 78.44 degree are created at (111), (002), (022), (113) and (222) planes, respectively and compared with ICSD, powder diffraction card of MgO file No. 43-1022. Furthermore, Mg(OH)2 phase is not seen in XRD patterns which emphasis in high purity.

The results of XRD for microwave method and sol-gel route have sharp peaks which indicate the homogenous crystallinity, while the diffraction peaks of MgO nanoparticles prepared by sol-gel are slightly broadened which is return to a small size of nanoparticles.

The average crystalline size was determined by Scherrer formula [10] given in Eq. (1)

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \quad \ldots \quad (1) \]

Where: D represents the average size of crystalline, while \( \lambda \) represents wavelength of X-ray, \( \beta \) is FWHM (Full Width at Half Maximum), and \( \theta \) is the angle of Bragg diffraction. While D represent the average size of crystal calculated by the diffraction peaks. It can be seen that 67 nm for the sample synthesized using microwave method and at 33 nm for the sample synthesized by sol-gel route.

![Figure 1: XRD patterns for Magnesium Oxide for microwave method, the blue line is Mg(OH)2 and the green line is MgO.](image-url)
3.2 Morphological analysis

Figure 3 and Figure 4 demonstrate the images of FESEM examination for MgO nanoparticles synthesized via the microwave and sol-gel methods, respectively. Figure 3. (a) and (b) demonstrate the images of FESEM examination for MgO nanoparticles synthesized via the microwave method, they have a particle size about 72 nm. The MgO nanoparticles have an irregular shape (nano sheets-like structure) resulting the agglomeration of MgO nanoparticles. While Figure 4. (a) and (b) evinces that the images of FESEM for MgO nanoparticles prepared by sol-gel method reveal a fine crystalline, nano spherical shape with a grain size about 50 nm.

(a) Under 1 µm and (10.00 KX) magnification   (b) Under 200 nm and (50.00 KX) magnification

Figure 3: FESEM images for MgO nanoparticles prepared by microwave method.
3.3 Specific surface area measurement

Specific surface area for MgO nanoparticles was measured by Brunauer-Emmett-Teller (BET). The values of specific surface area, particle size (from FESEM), Density (from experimental results of XRD) for MgO nanoparticles synthesized by microwave and sol-gel methods are given in Table 1.

| Synthesized method | Specific surface area (m²/g) | Particle size (nm) | Density (g/cm³) |
|--------------------|-------------------------------|--------------------|-----------------|
| Microwave method   | 41.0458                       | ≈ 72               | 3.59            |
| Sol-gel route      | 190.6529                      | ≈ 50               | 3.56            |

Table 1. Shows that the size of MgO nanoparticles for the sol-gel route is smaller than that for the microwave method, and the larger specific surface area is for the MgO nanoparticles synthesized by sol-gel route. The different in heating causes a dissimilar rate in solution vaporization and difference in the concentration of reactant in the liquid phase. This intern causes a different of nanoparticles sizes, particle shape and morphology of MgO prepared via sol-gel and microwave route. This difference is depending on the fundamental of sol-gel and microwave such as heating, homogeneous distribution of temperature or quenching.

Comparing the results of specific surface area S_{BET} with the average crystalline size obtained from XRD analysis, it is revealed that the more specific surface area, the less crystalline size as shown in Table 2. These results agreed with [11].

Figure 4: FESEM images for MgO nanoparticles prepared by sol-gel method.
Table 2: The difference between the values of particles size of MgO

| Synthesized method    | \( D_{XRD} \) (nm) | \( S_{BET} \) (m\(^2\)/g) |
|-----------------------|---------------------|-----------------------------|
| Microwave method      | 67                  | 41.0458                     |
| Sol-gel route         | 33                  | 190.6529                    |

3.4 FTIR Spectra

FTIR examination was carried out for MgO nanoparticles synthesized by the microwave and sol-gel routes as shown in Figure 5 and Figure 6 respectively. For microwave method, the observed strong band at 3695 cm\(^{-1}\) according to the \((O-H)\) stretching mode of hydroxyl groups which were presented on the surface because of the moisture. While the peak observed at 1423 cm\(^{-1}\) was returned to the bending vibration of water molecules. The main peak at 424 cm\(^{-1}\) attributed to the formation of Mg–O vibrations. While, for sol-gel method, the peak at 3672 cm\(^{-1}\) created according to \((O-H)\) stretching mode of hydroxyl groups were presented on the surface because of the moisture. The peak exhibited at 1454 cm\(^{-1}\) was created due to the bending vibration of water molecules. The main peak observed at 413 cm\(^{-1}\) due to the formation of Mg–O vibrations [12, 13].

Figure 5: FTIR peaks of MgO nanoparticles synthesized via the microwave route.
Figure 6: FTIR peaks of MgO nanoparticles synthesized via the sol-gel route.

4- Conclusions
Magnesium oxide nanoparticles were synthesized via two different routes, microwave route and sol-gel route. The characteristics of the synthesized MgO nanoparticles were examined using FESEM, BET XRD and FTIR. The results of XRD for microwave route and sol-gel route demonstrated sharp peaks which indicate the homogenous crystallinity, but there are diffraction peaks of MgO nanoparticles prepared by sol-gel which are slightly broadened due to a small size of nanoparticles. The size of MgO nanoparticles for the sol-gel route was smaller than that for the microwave method. The specific surface area of MgO nanoparticles compared with sol-gel was larger than that for MgO with microwave. The average crystalline size and particle size were found to be at 67 nm and 72 nm according to XRD and FESEM, respectively (for microwave method), and at 33 nm and 50 nm determined using XRD and FESEM, respectively (for sol-gel route). The FESEM images for MgO nanoparticles prepared by microwave method had an irregular shape, but the MgO nanoparticles synthesized using sol-gel route were found in a nano spherical shape. FTIR examination demonstrated that the presence of Mg-O in the sample.

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