Sol – Gel synthesis and characterization of magnesium peroxide nanoparticles

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Abstract. Magnesium peroxide is an excellent source of oxygen in agriculture applications, for instance it is used in waste management as a material for soil bioremediation to remove contaminants from polluted underground water, biological wastes treatment to break down hydrocarbon, etc. In the present study, sol-gel synthesis of magnesium peroxide (MgO_2) nanoparticles is reported. Magnesium peroxide is odourless; fine peroxide which releases oxygen when reacts with water. During the sol-gel synthesis, the magnesium malonate intermediate is formed which was then calcinated to obtain MgO_2 nanoparticles. The synthesized nanoparticles were characterized using Thermo gravimetric –Differential Thermal Analysis (TG- DTA), X-Ray Diffraction studies (XRD) and High Resolution Transmission Electron Microscope (HRTEM). Our study provides a clear insight that the formation of magnesium malonate during the synthesis was due to the reaction between magnesium acetate, oxalic acid and ethanol. In our study, we can conclude that the calcination temperature has a strong influence on particle size, morphology, monodispersity and the chemistry of the particles.

1. Introduction

Magnesium oxide has extensive applications in the detection and remediation of chemical waste and warfare agents [1]. It is also used as an additive in heavy fuel oils [2]; reflecting and anti-reflecting coatings [3] in optical applications; and is used as the substrate in superconducting and ferroelectric thin films [4-6]. Besides, magnesium oxide has also shown a promising application in catalysis applications of many organic reactions [7-12]. The properties of novel MgO are further magnified when its size is reduced to nanoscale. Many synthesis routes like sol-gel, hydrothermal, flame spray pyrolysis, laser vaporization, chemical gas phase deposition, combustion aerosol synthesis, aqueous wet chemical, and surfactant methods have been studied for nano-size synthesis of MgO [13-28]. But other forms of magnesium nanoparticles like MgOH and MgO_2 were given less importance because their applications are still unknown in many fields [29].

For a long time, MgO was believed to be among the least polymorphic solids[30]. Experimental simulation also predicted that MgO remains non-metallic up to extremely high pressure (20.7 TPa) [30, 31], making it to our knowledge the most difficult mineral to metalize. Thermodynamic

equilibriain the Mg-O system at 0.1 MPa shows that only MgO is a stable compound synthesized, though metastable compounds (MgO_2, MgO_4), which can be prepared at very high oxygen fugacities [32-34]. In the experiment performed by Qiang Zhu *et al*, two new stable compounds (MgO_2 and Mg_3O_2) has been found to exhibit interesting crystal structures with unusual chemical bonding and insulating and semiconducting electronic structures, respectively [35].

As magnesium peroxide is a stable oxygen releasing compound than Mg_3O_2, it can be used in agriculture to improve soil quality and in environmental industries as a bioremediation agent that converts contaminated soil into a fertile soil [36, 37]. In certain circumstances MgO_2 has also been shown to inhibit growth of bacteria. For example, the growth of sulfate –reducing bacteria can be inhibited in an environment containing MgO_2[38]. The nano form of MgO_2 can be used to enhance the oxygen releasing ability of the compound [39] and thereby increase its potentiality to be used in enormous applications. In our study, we had synthesized magnesium peroxide nanoparticles (MgO_2) by simple sol-gel method using magnesium acetate as precursor.

2. Experimental methods

2.1 Chemicals used

The commercially available magnesium acetate (98% pure) was obtained from Alfa Aesar, oxalic acid (99.5% pure) and ethanol (99.9%) from Merck was used in this reaction without further purification.

2.2. Synthesis of MgO_2 nanoparticles.

AnEquimolar ratio of magnesium acetate and oxalic acid were prepared separately by dissolving the salts in ethanol before they were mixed at 300rpm. The formation of gel starts immediately after mixing. Due to the addition of gelating agent, the sol of precursor dissolved in solvent forms a three dimensional network of magnesium through three major steps that were hydrolysis, polycondensation and thereafter gelation. After this, the gel was allowed for aging for about 12 hours in order to increase the thickness of the gel. Then the above aged gel was dried in hot air oven for about 24 hours at 100^{o}C in order to remove impurities through evaporation [13, 40]. The obtained powder was then calcinated at 600°C for 2 hours to obtain MgO_2 nanoparticles. The calcination was done in a box furnace (Sentrotech ST-1200C-7812) at a heating rate of 5°C/min. The calcination temperature was fixed by Thermo Gravimetric-Differential Thermal Analysis and the calcinated MgO_2 nanoparticles were characterized by X-Ray Diffraction spectroscopy for phase confirmation and High Resolution Transmission Electron Microscope for morphological analysis. Figure 1 shows the flow chart of magnesium peroxide nanoparticles synthesis by sol-gel method.

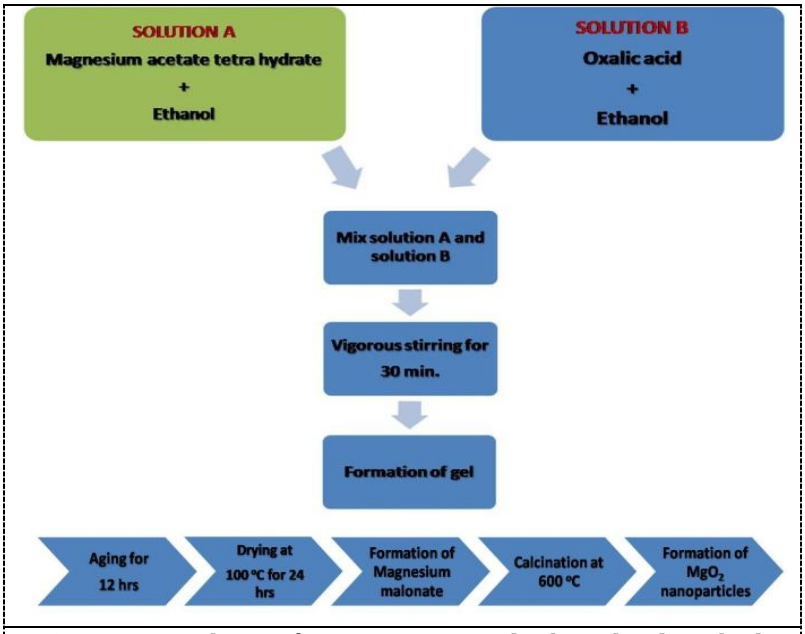

Figure 1: Synthesis of MgO_2 nanoparticles by sol-gel method.

2.3. Characterization of MgO_2 nanoparticles

The thermal analysis was carried out with a Thermo Gravimetry Analysis (TGA, ***S II TG/DTA 6300***) which will heat the sample up to 1200°C to find out thermal degradation of the sample. The TG-DTA was conducted at a heating rate of 5°C/min in nitrogen atmosphere. The phase purity and crystallinity of the MgO_2 nanoparticles were determined by X-ray diffraction (XRD) recorded on an X-ray Diffractometer system (***RIGAKU X ray diffractometer***). High resolution transmission electron microscopy (HR-TEM) measurement and the SAED pattern were studied using a HR-TEM, ***Tecnai T30 G^2 S-Twin, FEI Company*** which has a point resolution 0.24nm and its magnification ranges from 25x – 1030kx.

3. Results and Discussions

Sol–Gel method is a wet chemical technique widely used in the fields of materials science to synthesize ceramics with an intermediate stage. It is the precursor that, by its chemistry, leads the reaction towards the formation of either colloidal particles or polymeric gels [40]. In our experiment, the magnesium acetate precursor reacts with oxalic acid and ethanol to give magnesium malonate and the excess volatile substances in the reaction gets evaporated during aging and drying process [Equation 1]. Due to high temperature calcination at 600°C, the magnesium malonate gets transformed into magnesium peroxide [equation 2].

$$Mg\,(CH_3COO)_2 + C_2H_2O_4 + C_2H_5OH \longrightarrow Mg.\,[CH_2\,(COO)_2] + C_2H_2O_4\uparrow + C_2H_5OH\uparrow \quad (1)$$

$$Mg.\,[CH_2\,(COO)_2] \xrightarrow{600^oC} MgO_2 \text{ nanoparticles} \quad (2)$$

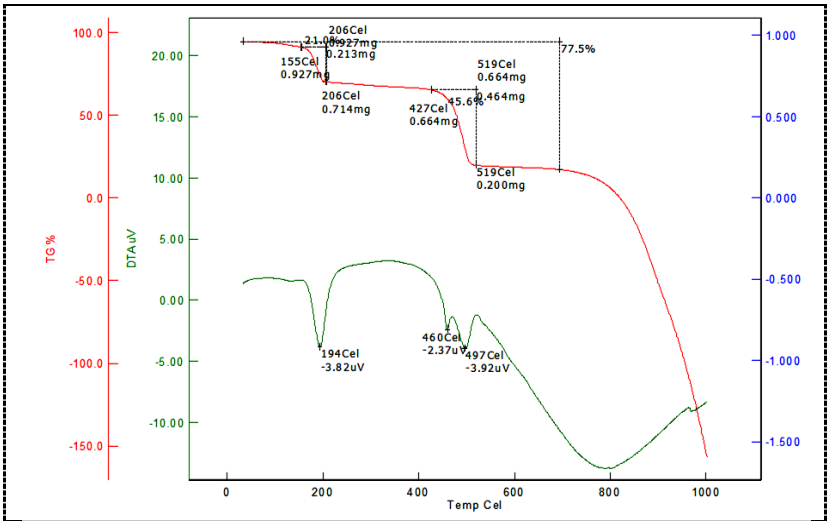

Figure 2: TG-DTA of pre calcinated magnesium malonate.

The TG curve of the compound shows the thermal decomposition in three stages. The water molecules get evaporated completely during drying of pre calcinated powder after aging in sol- gel process as shown in Fig 2. Dehydration occurred in the first stage (155-206 ^{o}C) in which the carboxyl molecules from the malonate group were lost due to decarboxylation (equation 3) [41]. After the first degradation, the end product contains unstable Mg. (CH_2) and it was degraded at 427 – 519 ^{o}C, in the second stage (equation 4). Though complete weight loss observed at 1000°C, we were able to study the effect of calcination at lower temperature (< 1000°C) with the intention of controlling the particle size and morphology [42, 43]. But at low temperature, calcination ended in the formation of unstable oxide (equation 5). MgO_2which was formed were confirmed by X-ray diffraction studies and displayed in figure 3. The thermal decomposition scheme is exemplified below

$$Mg.\,[CH_2\,(COO)_2] \xrightarrow{155\text{ -}206\ ^{o}C} Mg\,.\,(CH_2) + 2\,CO_2 \quad \text{(First decomposition)} \qquad (3)$$

$$Mg\,.\,(CH_2) \xrightarrow{427\text{ -}519^{o}C} Mg + CH_2 \quad \text{(Second decomposition)} \qquad (4)$$

$$Mg + O_2 \xrightarrow{600\ ^{o}C} MgO_2 \quad \text{(Third decomposition)} \qquad (5)$$

In the experiment performed by Davoodnia *et al*, the first decomposition of pre calcinated sample was found to be 359°C. The reason for this high temperature for the first decomposition was due to the usage of magnesium nitrate as a precursor in the sol-gel method. As the nitrate bond is very strong, only high temperature can break that bond to form stable oxides of magnesium [12]. But in our experiment, we can able to get first decomposition of the compound at 155°C due to the presence of magnesium acetate as the precursor in the sol-gel reaction. As the first decomposition is at l55°C, all the subsequent decomposition also occurs at low temperature compared to the literature. Then the sample is subjected to X-ray diffraction studies in order to confirm the crystalline phases of the pre calcinated and the calcinated sample.

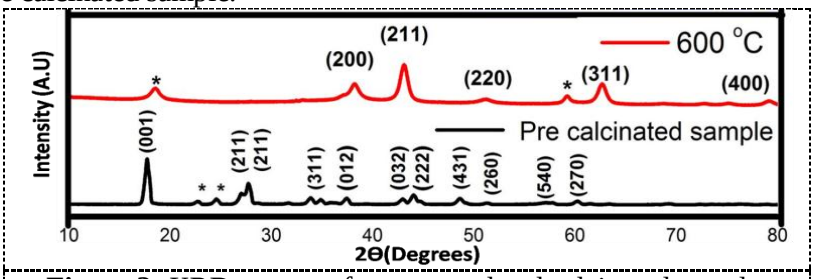

Figure 3: XRD spectra of as prepared and calcinated sample.

The * symbol in certain peaks indicates that those peaks are due to impurity in reaction atmosphere or due to unreacted components in the reaction mixture.

Figure 3 shows the XRD spectra for the formation of magnesium malonate in pre calcinated samples and the formation of MgO_2 nanoparticles in the calcinated sample at 600°C. The formation of magnesium malonate (PDF 24-1794) in pre calcinated sample is due to the reaction between the solvent (ethanol) and the gelating agent used (oxalic acid). The XRD peak of magnesium malonate was suppressed in the calcinated sample, which indicates the formation of magnesium peroxide. The XRD peak of the calcinated sample at 600 ^oC was matching with the MgO_2 (PDF 75-1585) crystal structure with some peak shifts. The peak shifts were due to the presence of certain impurities in the samples.

In the experiments performed by Stengl *et al*, Davoodnia *et al* and Athar *et al*, magnesium hydroxide [PDF 45-0946] is formed as the pre calcinated sample which was subjected to high temperature treatment up to 1000°C for several hours to get magnesium per oxide and magnesium oxide [12, 44, 45]. But in our experiment, the hkl (Miller indices) planes of magnesium malonate and magnesium peroxide is perfectly matching with the JCPDS (Joint Committee on Powder Diffraction Standards) files of the compound and the final product is obtained at low temperature (600°C) than compared to the above literatures.

The sample is then subjected to HRTEM for structural analysis. Figure 4 (a) shows the HRTEM micrograph of pre calcinated sample. It shows that the magnesium malonate formed are porous due to the evaporation of volatile compounds during drying process in sol-gel method at 100 ^oC. The SAED pattern [fig. 4(b)] reveals that the magnesium malonate is polycrystalline in nature as there are only two rings without proper spots for crystal pattern which is consistent with the result reported by Stengl *et al* and Gedanken *et al*[44, 46].The HRTEM micrograph of calcinated MgO_2 nanoparticles [fig. (c)] at 600°C shows a spherical morphology, which is agglomerated with each other due to high temperature. At 20nm scale, we observe that there is no porous structure in the calcinated samples. The calcination of pre calcinated magnesium malonate powder breaks the micro particles into pieces to form nanoparticles of magnesium peroxide [45].

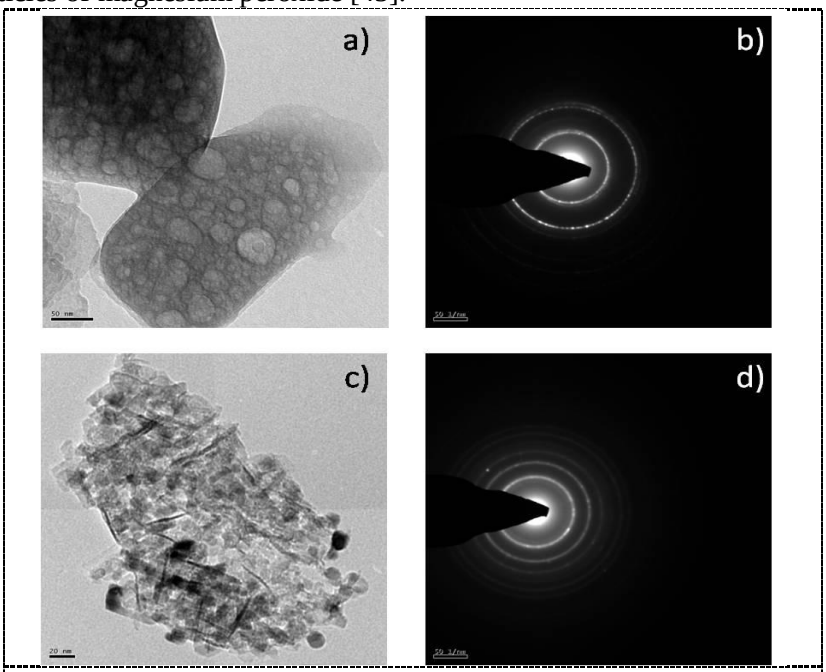

Figure 4: a) HRTEM micrograph of magnesium malonate b) SAED pattern of magnesium malonate c) HRTEM micrograph of magnesium peroxide d) SAED pattern of magnesium peroxide.

Further calcination of pre calcinated sample at higher temperature will lead to the formation of highly stable MgO nanoparticles[13]. We recommend that increasing the calcination time and calcinating the sample in ambient atmosphere can help to obtain monodispersed MgO_2 nanoparticles and to avoid agglomeration [47]. By obtaining monodispersed nanoparticles, it can be used in bioremediation applications and in improving soil quality on par with bulk magnesium peroxides.

4. Conclusion

In this work, MgO_2 nanoparticles have been synthesized by simple sol – gel method using inorganic precursor such as magnesium acetate, oxalic acid as gelating agent and ethanol as solvent. Initially, magnesium malonate was formed which was due to the inorganic precursor and shows that precursor plays a major role in the formation of nanoparticles. Further, the as prepared samples were calcinated at 600°C in order to obtain MgO_2 nanoparticles, which show that calcination temperature plays a pivotal role in the formation of the end product as well as the morphology of the nanoparticles. Thus the synthesized MgO_2 nanoparticles can be used as an excellent oxygen source in agriculture and in environment application.

5. References

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