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Nucleophilic Chemistry of the Synthesized Magnesium Oxide (Magnesia) Nanoparticles via Microwave@sol-gel Process for Removal of Sulfurous Pollutant

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ABSTRACT

In this scientific research, magnesium oxide (MgO) nanoparticles were synthesized from magnesium nitrate and ammonium solutions via microwave@sol-gel process. The structure and the morphology of the synthesized nanoparticles has been identified and characterized by X-ray diffraction (XRD), N_2-BET (Brunauer-Emmett-Tell), scanning electron microscopy (SEM) and fourier transform infrared (FTIR) techniques. The crystallite size of nano MgO was in the range of (100 nm (and surface area of 596.39 m^2/g. The (2-chloro ethyl phenyl sulfide) 2-CEPS are a sulfurous pollutant. This compound can cause the contaminations of environment. In this survey, we used MgO nanoparticles for removal of 2-CEPS molecule. The results of UV/Vis irradiation for the weight ratio of 1:40 (2-CEPS: MgO nanoparticles) at ambient temperature emphasized that 2-CEPS molecule has the highest amount of removal about 61% and 70% by nanoparticles in the isopropanol and n-heptane solvents after 8 hours, respectively. Although, for the weight ratios of 1:10, 1:20 and 1:30 very lower degradation of the sulfurous pollutant (from the same conditions) was observed. Elimination single product; i.e. phenyl vinyl sulfide (PVS) has been identified via GC-MS analysis.

Keyword: Magnesium oxide nanoparticles; Microwave@sol-gel; 2-CEPS; Removal; UV/Vis irradiation.

1. INTRODUCTION

The surface area of metal oxide plays an important role in different reaction occurring in nature and in industrial processes. These compounds are found to be promising adsorbents for the degradation of environmental pollutants [1]. Magnesia (MgO) is a basic oxide with direct band gap of 7.8 eV and isoelectric point between 12.1 and 12.7. It is a unique solid catalyst that is prepared in widely

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variable particle sizes and shapes. In Figure 1, the structure of MgO crystal is shown. In this structure, cations and anions occupied octahedral areas and the crystal focuses respectively [2, 3]. MgO nanoparticles are functional materials that have been widely used in various areas and recently it has been reported that MgO has a good performance for detoxification and removal of sulfurous pollutants [1]. The one pioneer in this section is wagner and Klabunde [4, 5] who demonstrated that nano-MgO exhibits high activity against sulfurous pollutants. Compared with TiO_2, ZnO, CdO, Al_2O_3, CuO and other kinds of solid nanomaterials, nano-MgO has the advantage of being prepared from readily availableand economical precursors and solvents, and therefore has considerable potential as a solid material under simple conditions.

There are several methods for the synthesis of nanoscale MgO, including sol-gel [2], gas phase condensation [2], laser ablation [2], flame processing [6], sonochemical, microwave plasma [7], hydrothermal synthesis [8], electric dispersion reaction, combustion synthesis, spray pyrolysis, mechanochemical synthesis, reverse micelle and finally ultrasonic process [9-11]. In this research, we indicated the synthesis of MgO nanoparticles by microwave@sol-gel process. The characterization of synthesized MgO particles (such as surface reactivity, structure and morphology) and its reaction via sulfurous compound were studied. Then, the performance of synthesized MgO particles in the removal of 2-CEPS (2-chloro ethyl phenyl sulfide: a sulfurous pollutant) molecule with the different weight ratios and in the different solvent was investigated.

2. EXPERIMENTAL

2.1. Materials

$Mg(NO_3)_2{\cdot}6H_2O$, MgO (bulk) and ammonia solution (25%) are purchased from Merck Co. (Germany). n-heptane, isopropanol, toluene and 2-CEPS (2-chloroethyl phenyl sulfide) form Sigma-Aldrich Co. (USA), were used as received.

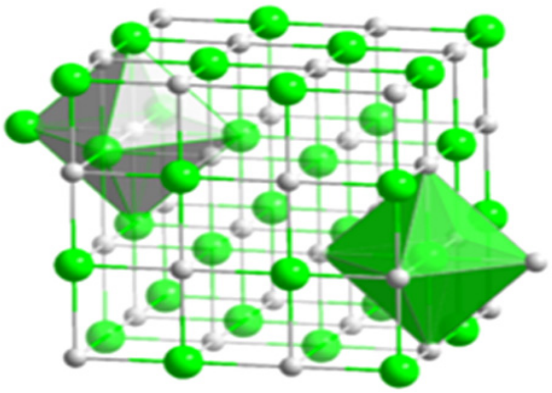


Figure 1: *Structure of MgO crystal.*

2.2. Synthesis of MgO nanoparticles with Microwave@sol-gel process

MgO nanoparticles were synthesized according to the following procedure: 0.1 mol/L magnesium-nitrate solution was prepared by dissolving $Mg(NO_3)_2{\cdot}6H_2O$ in de-ionized water. The pH of 200 ml deionized water was adjusted to 10.5 by the addition of ammonia solution (25%), and to this solution, 0.1 mol/L magnesium nitrate solution was added dropwise with vigorous stirring. During the addition, the pH of the mixture decreased due to the hydrolysis of the salt. The pH was maintained at 10.5 by the controlled addition of ammonia solution. After completion of the precipitation procedure, the $Mg(OH)_2$ gel was transferred into microwave set (350 W) for 15 min. During the microwave irradiation, the temperature of the solution reached 80°C. The resulting precipitate was then cooled to room temperature, filtered, and washed with deionized water more than five times. The obtained solid was dried at 120°C for 60 min and calcined at 500-550°C for 90-120 min to give the product. The final white powder was obtained.

2.3. Characterization of MgO nanoparticles

The microwave set (CE250, Samsung Korea) was used for synthesis of MgO nanoparticles. X-ray diffraction (XRD) analysis was carried out on a Philips X-ray diffractometer using CuKα radiation (40 kV, 40 mA and λ=0.15418 nm). Samples were scanned at 2°/min in the range of 2θ = 10-100°. Nitrogen Adsorption Isotherm was obtained on a quantachrome nova 1200 multipoint BET apparatus

using approximately 0.1 g of sample for measurement. Immediately prior to the N_2 adsorption sample was vacuum degassed at 100 for 1 h.The morphology of the products was carried out using Field Emission Scanning Electron Microscope (SEM, LEO-1530VP). The IR spectrum was scanned using a Perkin-Elmer FTIR (Model 2000) in the wavelength range of 400 to 4000 cm^{-1} with KBr pellets method. To investigate the reaction between MgO nanoparticles catalyst and the sulfurous compound of 2-CEPS (2-CEPS/MgO nanoparticles), the samples were prepared according to the following method:

The absorption spectrum of 2-CEPS in the presence of different ratios of MgO particles were examined with Lambda UV/Vis spectrometer in the range of 200-300 nm. For the investigation of UV/Vis spectrum, 10 µL of sulfurous compound (2-CEPS), 5 mL isopropanol or n-hepane for solvent and 10 µL toluene for internal standard were added to the 50 mL Erlenmeyer flask and the mixture were stirred for 8 h at ambient temperature (25±1°C). Then, 5 to 7 µL of supernatant was removed and the reaction mixture at different times (for investigation the effect of the time in the degradation) was spilled in the UV cell (filled two-thirds of total volume of different solvents and for investigation the effect of the solvent in the degradation). For the identification of destruction product, the best sample (10 µL solution was extracted and injected to column) was analyzed via GC-MS instrument Varian Star 3400 CX gas chromatograph with a flam ionization detector (FID). A fused-silica capillary column DB 5 MS, 101 mic, 30 m× 0.25 mm was used. The carrier gas was helium with a flow rate of 1 $mL.min^{-1}$. The initial and final temperature of the oven was programmed to 60°C (hold for 4 min) and 230°C, respectively. To reach the final temperature (after 4 min); the temperature was increased at a rate of 20 min/°C.

3. RESULT AND DISCUSSION

3.1. X-ray diffraction (XRD)

X-ray diffraction pattern of the synthesized MgO particles is shown in Figure 2. The Scherrer equation is used in X-ray diffraction and crystallography to correlate the size of sub-micrometer particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern (1):

$$d= 0.94\lambda/\beta\cos\theta \quad (1)$$

Where d is the crystal size, λ is wavelength of X-ray source, β is the full width at half maximum (FWHM), and θ is the Bragg diffraction angle. The average size of nanoparticles calculated from Scherrer equation is reported about 43 nm.

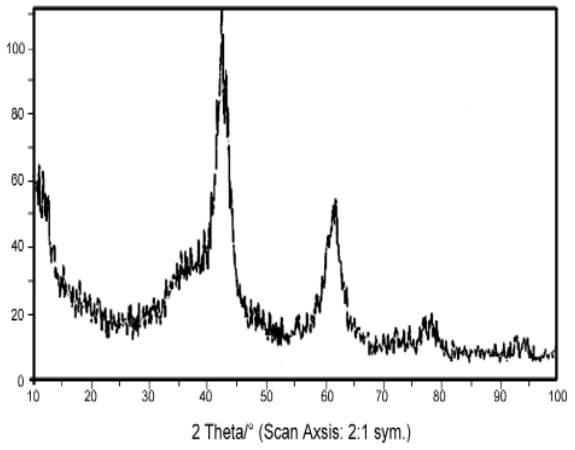


Figure 2: *XRD pattern of MgO nanoparticle.*

3.2. Nitrogen adsorption analysis of MgO nanoparticles

The structure properties of MgO nanoparticles were obtained from the nitrogen adsorption isotherm or Brunauer-Emmett-Tell (BET) and are listed in Table 1.

Table 1: *Properties of synthesized MgO nanoparticles.*

BET surface area(m^2/g)	596.39
Average pore diameter(nm)	2.8094
Total pore volume(cm^3/g), ρ/ρ_0=0.502	0.2573

3.3. SEM analysis

SEM images were used to indicate the morphology and size distribution of the MgO powders (micro and

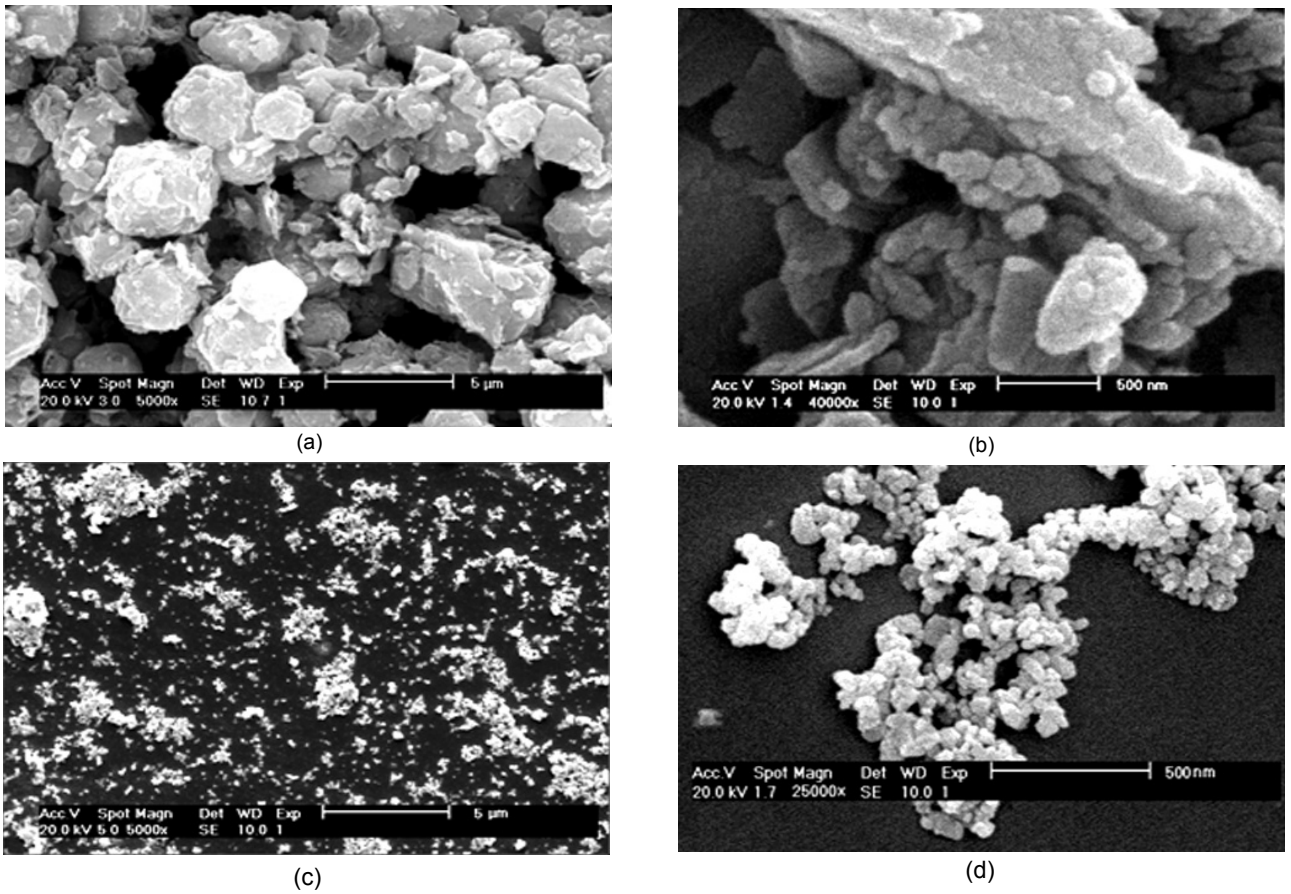


Figure 3: *SEM images with different magnification (a) and (b) MgO microcrystals, (c) and (d) MgO nanocrystals.*

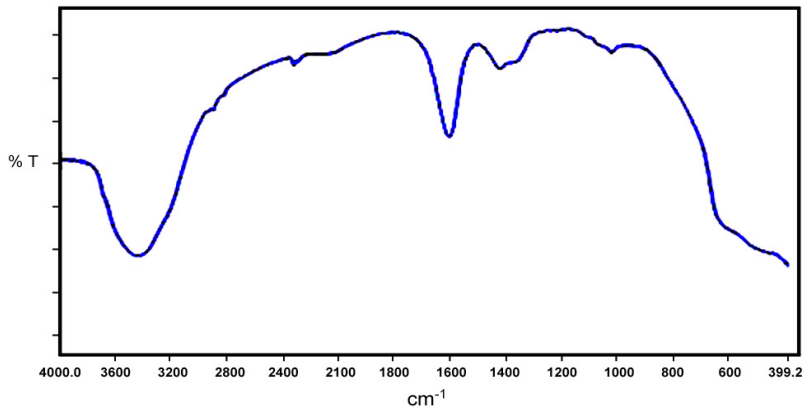


Figure 4: *FTIR spectrum of MgO nanoparticles.*

nano crystals). Figures 3a, 3b, 3c and 3d show the SEM photographs of technical grade of MgO microparticles and synthesized MgO nanoparticles with different resolution, respectively. The particle size of the MgO sample was typically less of 100 nm.

3.4. FTIR analysis

The FTIR spectra of the prepared MgO nanoparticles are shown in Figure 4. In these spectra, it can be observed apparently that strong band at 416 cm^{-1} associated with the characteristic

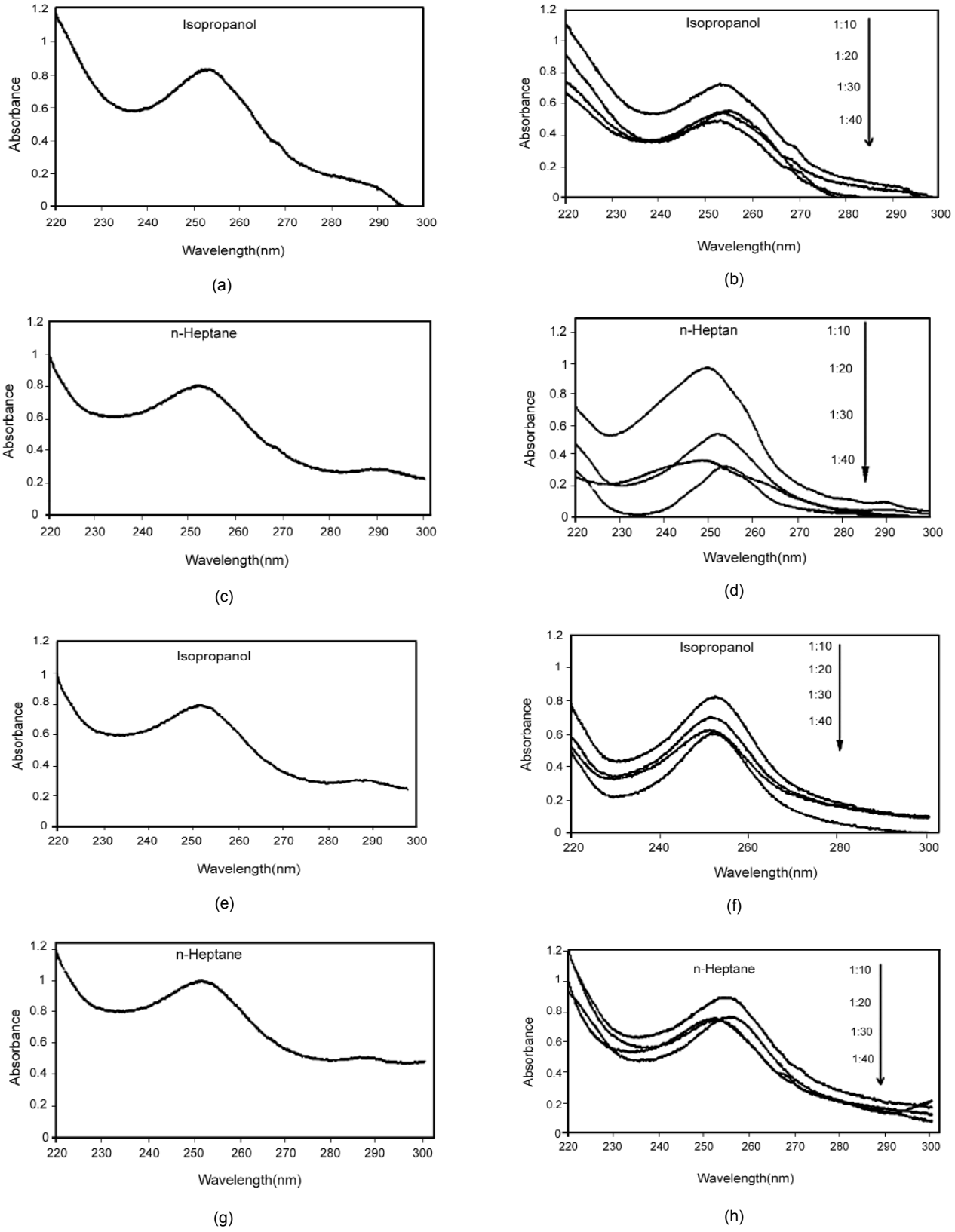


Figure 5: *UV/Vis spectrum of (a), (b), (c) and (d) MgO nanoparticles, (e), (f), (g) and (h) MgO microparticles.*

vibrational mode of symmetric octahedral of MgO. The absorption at 3425 cm^{-1} indicates that the presence of O-H group, which is probably due to the fact that the spectra were not recorded in situ and some readsorption water from the ambient atmosphere has occurred. The bands in the range of 1300-1700 cm^{-1} may be related to hydroxyl groups of molecular water at 1623 cm^{-1} and to NH_3 at 1446 cm^{-1}. These bands further confirm that the MgO phase can be indeed formed after combustion at 550°C.

3.5. Preparation of 2-CEPS/ MgO nanaoparticles

The adsorption/destruction of 2-CEPS molecule in the presence of MgO microcrystalline and nanocrystalline were studied in different weight ratios conditions and solvents by using UV/Vis spectrum. First, UV/Vis spectrum of the blank sample is taken. The blank sample is prepared with 10 µL of 2-CEPS, 5 mL isopropanol solvent and 10 µL toluene (Figure 5). Then, for the investigation reaction between 2-CEPS and MgO particles, 5, 50, 100 and 150 mg of MgO (nano and micro crystals) particles was added to blank solution, respectively. To study the effect of solvent type, the reaction of 2-CEPS with MgO particles in the same conditions is repeated and n-heptane was used instead of isopropanol. As can be seen from the spectrum, the absorption will be reduced after 8 hours. In table 2, the results of UV/Vis irradiation in the presence of different weight ratios and solvents were shown. Each UV/Vis spectrum is divided in two parts; part I) absorption in the range between 220 to 250 nm (Related to 2-CEPS) and part II) absorption above 250 nm (related to destructed product of 2-CEPS).

The results are show that the potential degradation of 2-CEPS in the non-polar n-heptane solvent is higher than the polar isopropanol. Thus, deduced that in the removal reaction, we have a competition between 2-CEPS molecule and isopropanol solvent to be occupied active sites of MgO particles catalyst that consequently, the adsorption reaction is reduced. On the other hand, n-heptane is an inert solvent. Due to there is any competition between it and the 2-CEPS, sulfurous molecule can be easily adsorbed via MgO particles.

3.6. GC-MS analysis

To understanding the composition of destruction product of 2-CEPS with MgO nanoparticles gas chromatography coupled with mass spectrometry (GC-MS) analysis was used (Figure 6). Destruction product resulting from removal of 2-CEPS is diagnosed at a retention time 3/80. The detector was set to scan a mass range of 28 to 135 m/z and 28 to 172 m/z for PVS and 2-CEPS (remaining), respectively. Thus, about 50% of the 2-CEPS as 2-hydroxy ethyl sulfide (2-HES) are adsorbed. This compound is not seen in the analysis, because that is directly connected on the catalyst surface and not be removed easily from the surface even if it be washed with dichloro methane solvent. Generally, with increasing the weights of MgO nanoparticles

Table 2: *The results of UV/Vis irradiation in the presence of different weight ratios and solvents.*

RATIOS	% removal/MgO microparticles		% removal /MgO nanoparticles	
solvent	isopropanol	n-heptane	isopropanol	n-heptane
BLANK	100	100	100	100
1:10	78.42	73.85	67.75	52.03
1:20	71.01	69.78	48.42	40.41
1:30	68.11	67.17	45.01	34.01
1:40	61.22	59.47	38.24	29.71

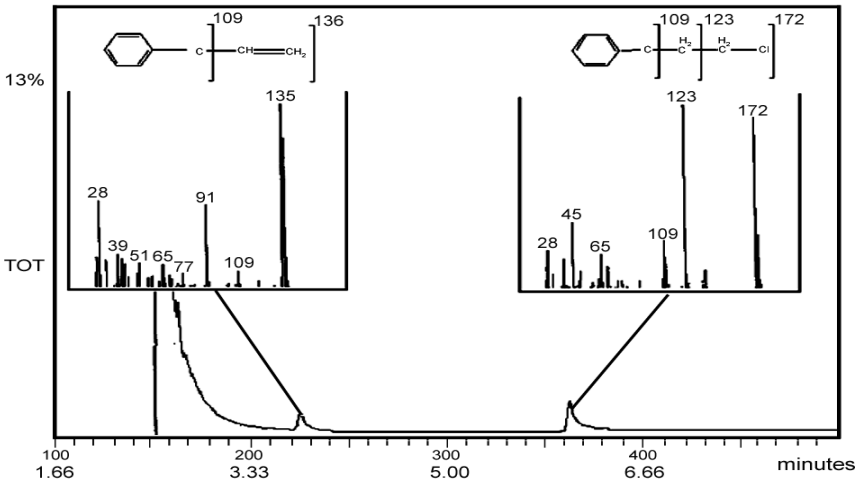
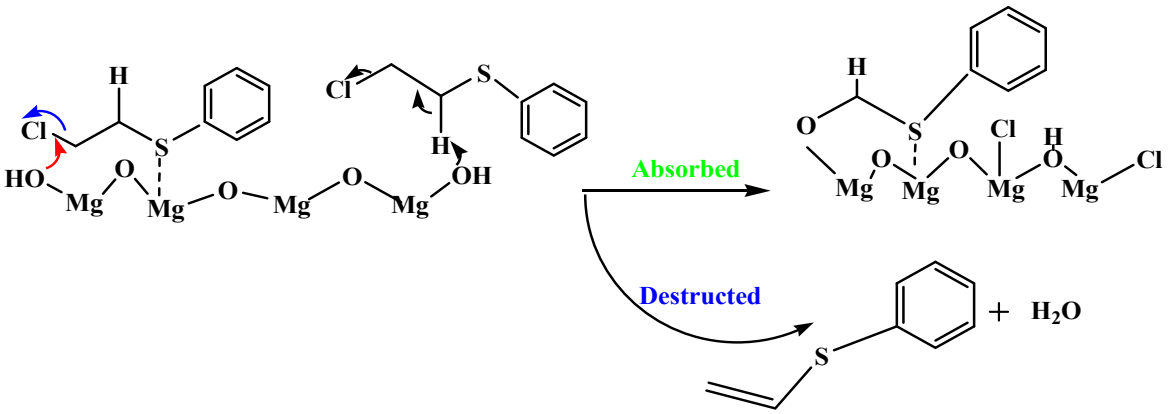


Figure 6: *GC-MS analysis results for reaction of 2-CEPS/MgO nanoparticles.*



Scheme 1: *Proposed mechanism for the adsorption and destruction 2-CEPS on MgO nanoparticles catalyst.*

to the 2-CEPS, higher values sulfurous compound can be adsorbed and destructed. Although, very little destruction of 2-chloroethyl phenyl sulfide was observed in the weight ratios of 1:10 and 1:20 of catalyst, in the 1:30 and 1:40 weight ratios, the destructing of sulfurous pollutant was accelerated and destructed product was also observed. After identification of the destruction product 2-CEPS with MgO nanoparticles catalyst, its proposed mechanism of adsorption and destruction of 2-CEPS in the presence of this nanocatalyst which is shown in Scheme 1. The reactions between the MgO nanoparticles and 2-chloroethyl phenyl sulfide has two sections:

Section I) adsorption reaction with nucleophilic attack the Mg atoms and the Bronsted acid sites (OH) of catalyst to the chlorine and sulfur atoms of 2-CEPS, respectivley. In this interaction, the chlorine atom in 2-chloroethyl phenyl sulfide will be removed (the dehalogenation reaction).

Section II) destruction reaction with nucleophilic attacks the Bronsted acid sites (OH) of catalyst to the hydrogen atom of 2-CEPS. In this interaction, water will be removed (the hydrolysis

reaction).

4. CONCLUSIONS

The potential of MgO particles (micro and nano crystals) for the destruction of 2-CEPS (a sulfurous compound) was reported. Magnesium oxide nanoparticles with high surface area (596.39m^2/g) were synthesized via a microwave@sol-gel process. In fact, with a simple and low cost method, fine particles with high performance were synthesized. The structure and morphology of particles were investigated by XRD, SEM and FTIR analyses. The results of UV/Vis irradiation for the weight ratio of 1:40 (sulfurous compound: nano MgO) emphasized that 2-CEPS molecule has the highest amount of the degradation about 61% and 70% with nanoparticles in the isopropanol and n-heptane solvents after 8 hours, respectively. On the other hand, the destruction reaction of 2-CEPS via MgO microcrystals has lower amount. Elimination single product; i.e. phenyl vinyl sulfide (PVS) has been identified via GC-MS analysis. This product has less toxic in compare to 2-chloro ethyl phenyl sulfide molecule.

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