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Synthesis and Characterization of $ZnCaO_2$ Nanocomposite Catalyst and the Evaluation of its Adsorption/Destruction Reactions with 2-CEES and DMMP

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ABSTRACT

In this work, $ZnCaO_2$ (zinc oxide-calcium oxide) nanocomposite were synthesized at different temperatures (500-700°C) by sol-gel method based on polymeric network of polyvinyl alcohol (PVA). The synthesized samples were characterized by SEM/EDAX, FT-IR and XRD techniques. It was found that synthesized nanocomposites have 1.62, 2.05 and 13.91%wt of CaO, respectively. The obtained results show that each particle of nanocomposite has been made of a CaO core which is completely covered by ZnO layers. The smaller average diameter of synthesized nanoparticles (at 600°C) calculated by XRD technique found to be 33 nm for prepared $ZnCaO_2$ nanocomposite. This compound has been used as adsorbing removal for agricultural pesticide. The 2-chloroethyl ethyl sulfide (2-CEES) and dimethyl methyl phosphonate (DMMP) are for the class of compounds containing phosphonate esters and sulfurous with the highly toxic that used such as pesticides, respectively. The adsorption/destruction reactions of 2-CEES and DMMP have been investigated by using $ZnCaO_2$ nanocomposite. Reactions were monitored by GC-FID (gas chromatography) and FT-IR techniques and the reaction products were characterized by GC-MS. The results of GC analysis for the weight ratio of 1:40 (2-CEES/DMMP: $ZnCaO_2$ nanocomposite) at room temperature showed that 2-CEES molecule is destructed about perfectly in the n-pentane solvent by nanocomposite after 12 hours and it changed to less toxic chemical hydrolysis and elimination products and identified via GC-MS (gas chromatography-mass spectrometry) instrument, were hydroxyl ethyl ethyl sulfide (HEES) and ethyl vinyl sulfide (EVS), respectively. On the other hand, the ^{31}PNMR analysis emphasized that 100% of DMMP molecule after 14 hours in the n-pentane solvent was adsorbed.

Keyword: $ZnCaO_2$ Nanocomposite; Sol-Gel; 2-CEES and DMMP; Adsorption/Destruction; ^{31}PNMR.

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1. INTRODUCTION

One of the first successful applications of nanotechnology was the use of oxides as catalysts for adsorption of toxic sulfurous and organo-phosphate. Recently, wurtzitic group-II oxides such as ZnO have attracted attention due to their potential applications in adsorption and destruction of toxic pollutants [1]. Heterostructures or alloys of ZnO with CaO [2] are important for band-gap tailoring, since it is possible to open up the energy band-gap from 3.4 eV [wurtzite (wz) ZnO] to almost more of 4 eV in $Ca_xZn_{1-x}O$ alloys [3, 4]. A suitable process for control of nanoparticles is using of sol-gel pyrolysis method [5]. In this research, the synthesis and characterization of $ZnCaO_2$ nano-composites via sol-gel pyrolysis method at temperatures 500, 600 and 700°C is reported. Then, we have focused our attention on the nano-composite due to good catalytic properties and high performance for the adsorption/destruction of the 2-CEES and DMMP molecules (Figure 1a and b). The 2-CEES and DMMP molecules are used for the class of compounds such as agricultural pesticides which containing and sulfurous phosphonate esters, respectively [6-13].

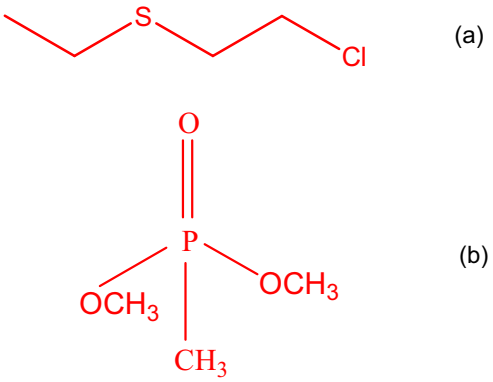


Figure 1: *Molecular structures of (a) 2-CEES and (b) DMMP.*

2. EXPERIMENTAL

2.1. Materials

$Zn(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, ethanol, poly vinyl alcohol (PVA) and phosphoric acid 85% (d= 1.5 g/mL), are purchased from Merck Co. (Germany). N-pentane, toluene, $CDCl_3$, 2-CEES (2-chloroethyl ethyl sulfide) and DMMP (dimethyl methyl phosphonate) form Sigma-Aldrich Co. (USA) were used as received.

2.2. Physical characterization

The morphology of the products was evaluated by using Emission Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM/EDAX, LEO-1530VP). The IR spectrum was scanned using a Perkin-Elmer FT-IR (Model 2000) in the wavelength range of 400 to 4000 cm^{-1} with KBr pellets method. X-ray diffraction (XRD) analysis was carried out on a Philips X-ray diffractometer using CuK_α radiation (40 kV, 40 mA and λ= 0.15418 nm). Sample were scanned at 2°/min in the range of 2θ = 10-90°.

2.3. Synthesis of $ZnCaO_2$ nanocomposite catalyst by sol-gel pyrolysis method

$ZnCaO_2$ nanocomposite was synthesized according to the following procedure: First, 100 ml ethanol/water solution with ratio of 50:50 for solvent was added to a 200 mL Erlenmeyer flask. Then, 87 g solvent that was prepared at previous stage was transferred to a cruicible. In the next step, 2 g $Zn(NO_3)_2.6H_2O$ and 2 g $Ca(NO_3)_2.4H2O$ were added to solution and stirred until the solution became clear. 9 g poly vinyl alcohol (PVA) was added to clear solution until 100 g sample to be produced. The sample was stirred vigorously for 1 h and the temperature slowly increased until at 80°C to form a homogeneous sol solution. The final gel was cooled and then calcined at 500, 600 and 700°C for 16 h.

2.4. Preparation of $ZnCaO_2$ nanocomposite/ 2-CEES sample

For each sample, 10 µL of 2-CEES, 5 mL n-pentane solvent and 10 µL toluene (internal standard) and 150 mg $ZnCaO_2$ nanocomposite were added to the 50 mL Erlenmeyer flask. To do a complete reaction

between catalyst and sulfurous compound, all samples were attached to a shaker and were shaked for about 0, 2, 4, 6, 8, 10 and 12 h. Then, by micropipette extracted 10 µL of $ZnCaO_2$ nanocomposite/2-CEES sample solutions and injected to GC and GC-MS (Varian Star 3400 CX, OV-101 CW HP 80/100 2m×1.8 in and DB 5 MS, 101 mic, 30 m×0.25 mm) instruments. Temperature program for GC: The initial and final temperature of the oven was programmed to 60°C (held for 4 min) and 220°C, to reach the final temperature(after for 4 min); the temperature was increased at rate of 20°C/ min for 13 min. Also, detector temperature was 230°C (Figure 2).

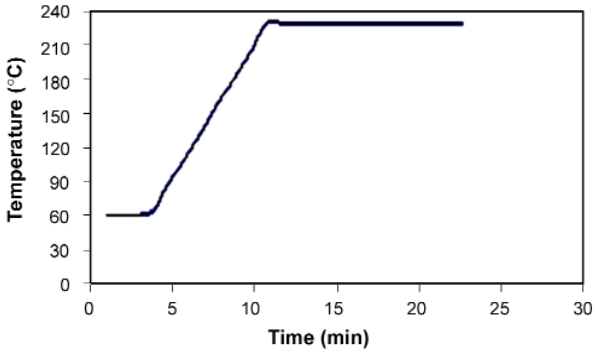


Figure 2: *The temperature program for GC set.*

2.5. Preparation of $ZnCaO_2$ nanocomposite/ DMMP sample

For investigation of the reaction $ZnCaO_2$ nanocomposite and DMMP, $ZnCaO_2$/DMMP sample were prepared according to the following method: For the preparation of the phosphoric acid solution blank (0.03 M), first, 0.05 mL phosphoric acid 85% (d= 1.5 g/mL) was diluted with 25 mL deionized water and injected to a capillary column and closed two tips by heat. Then, 37 µL DMMP, 10 mL n-pentane as solvent and 0.48 g $ZnCaO_2$ nanocomposite were added to the 50 mL Erlenmeyer flask and the mixture was stirred for 0, 1, 2, 3, 4, 5, 6 and 14 h at ambient temperature. In the next step, 1 mL solution was placed in centrifuge instrument (CAT.NO.1004, Universal) by 500 rpm for 5 min for doing the extraction operation. Now, 0.3 mL of the $ZnCaO_2$ nanocomposite/DMMP sample solution and 0.1 ml $CDCl_3$ were added to a NMR tube and capillary column was added to the tube for the blank. After that, the presence of the DMMP in the sample was investigated by the ^{31}PNMR) 250 MHz Bruker) instrument.

3. RESULT AND DISCUSSION

3.1. SEM/EDAX analysis

The SEM images with different magnification and EDAX analysis of the $ZnCaO_2$ nanocomposites at 500, 600 and 700°C are shown in Figures 3 and 4. This micrographs show that with increasing of calcination temperature, the particles size and the morphology of nanoparticles are changed. The results of EDAX analysis were emphasized that, percent of CaO (wt%) in the synthesized nanocomposites has increased (Table 1). On the other hand, the smaller of the particle size is corresponded to the synthesized nanocomposite at 600°C and forming as spherical.

3.2. FT-IR studies

FT-IR spectra of $ZnCaO_2$ nanocomposites at different temperature (500, 600 and 700°C) are shown in Figure 5. The peaks at 1630 and 1710

Table 1: *The results of EDAX analysis for the synthesized $ZnCaO_2$ nanocomposites.*

Temperature(°C)	ZnO(wt%)	CaO(wt%)	Average particle size
500	98.38	1.62	70 - 100
600	97.95	2.05	30 - 40
700	86.09	13.91	200 nm (diameter)

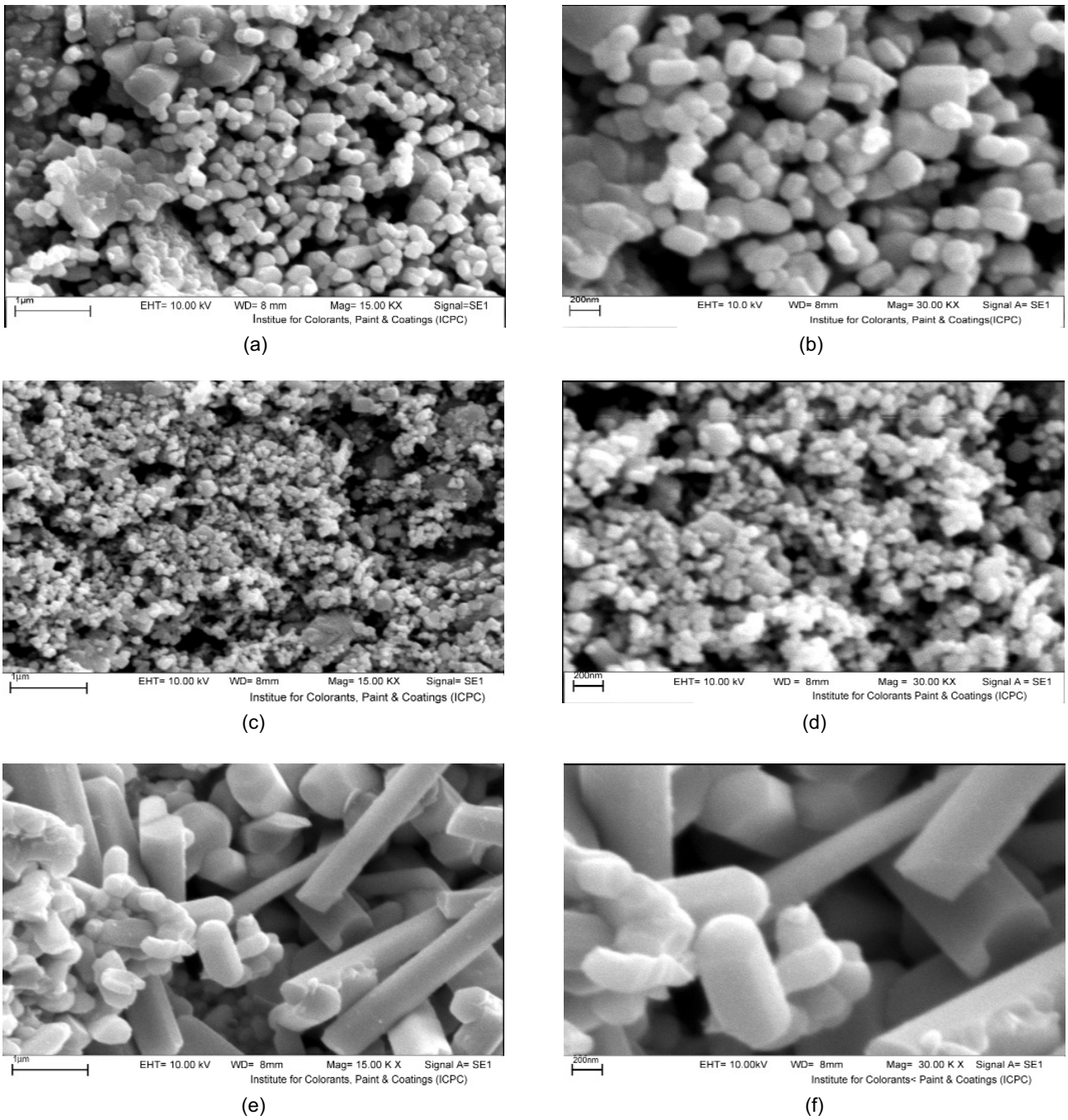


Figure 3: *SEM images of $ZnCaO_2$ nanocomposites, (a) and (b) 500°C, (c) and (d) 600°C, (e) and (f) 700°C with different magnification (15000X and 30000X).*

cm^{-1} are assigned to CO_2 absorbed on the surface of nanoparticles. The peaks at 1350 and 847 cm^{-1} are assigned to C-H and C-C bonding vibrations of organic impures in the synthesized sample, respectively. The peak around 3450 cm^{-1} is corresponded to (OH) stretching vibration. The strong absorbed peak around 450 cm^{-1} is corresponded to ZnO and CaO bonds.

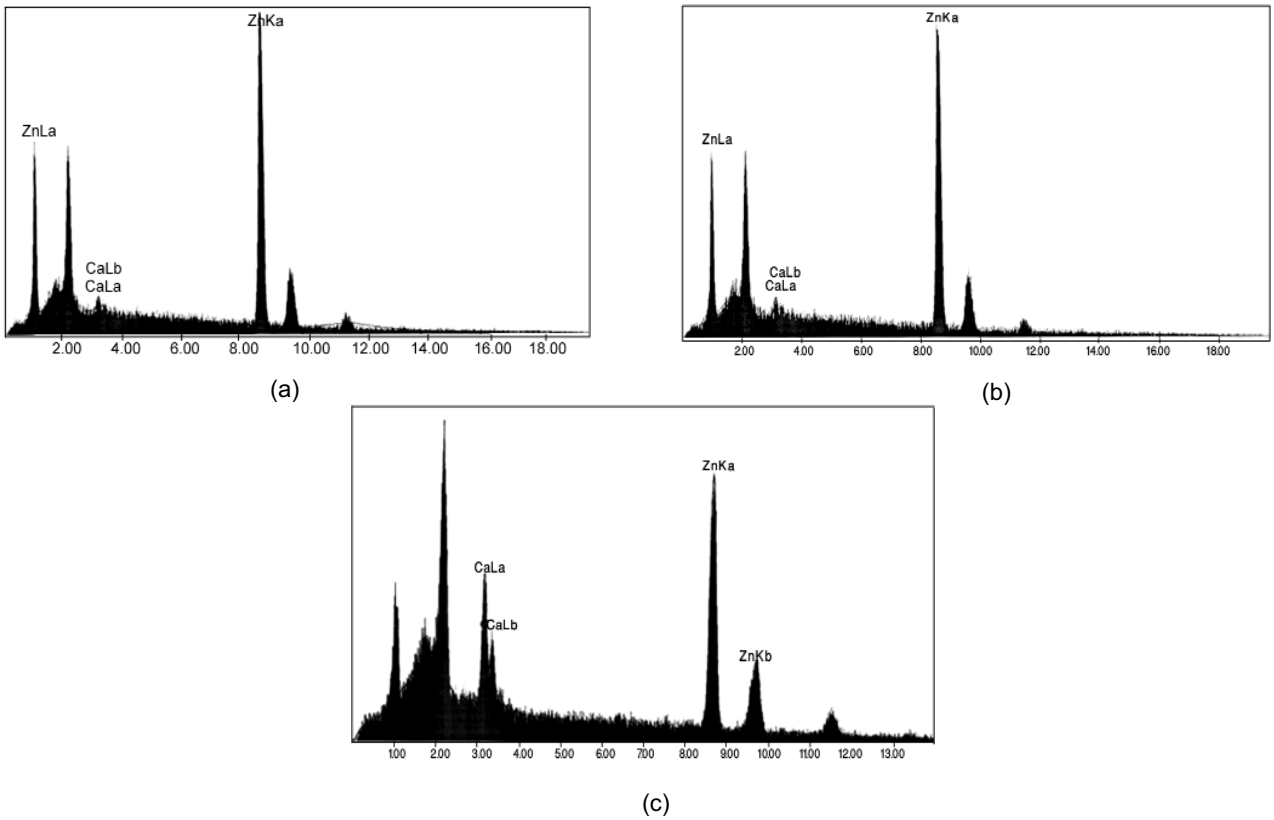


Figure 4: *EDAX analysis of $ZnCaO_2$ nanocomposites, (a) 500, (b) 600 and (c) 700°C.*

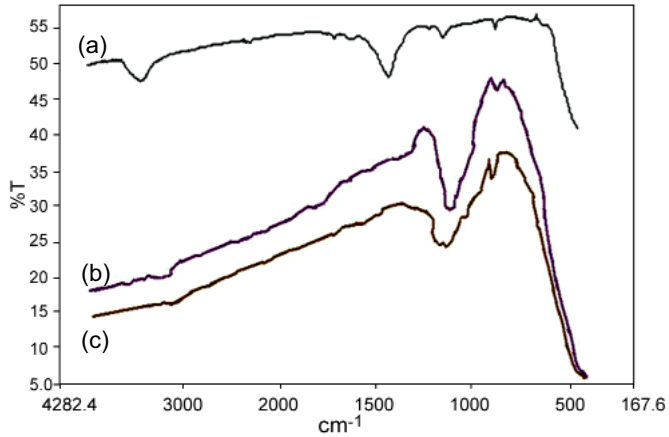


Figure 5: *FTIR spectra of $ZnCaO_2$ nanocomposite, (a) 500, (b) 600 and (c) 700°C.*

3.3. X-ray diffraction (XRD) study

The structure of prepared $ZnCaO_2$ nanocomposite at 500-700°C was investigated via X-ray diffraction (XRD) measurement (Figure 6). The average particle size of nanocomposite was investigated from line broadening of the peak at 2θ= 10-90° via using Debye-Scherrer formula (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 smaller average particles size by Debye-Scherrer formula was estimated to be 33 nm for 600°C. 2θ= 33.001°, 38.285°, 55.258°, 65.910°, 69.288 (black points) corresponded CaO nanoparticles (FCC phase) and 2θ= 31.72°, 34.4°, 36.24°, 47.52°, 56.6°, 62.8°, 66.3°, 67.9°, 69.1° corresponded ZnO nanoparticles. All diffraction peaks are indicating to the hexagonal phase with wurtzite structure for ZnO. After the characterization, obtained $ZnCaO_2$ nanocomposite (600°C) sample was used to study the interaction with 2-chloroethyl ethyl sulfide (2-CEES) and dimethyl methyl phosphonate (DMMP) at room temperature (25±1°C).

3.4. GC, FT-IR and GC-MS studies

The evaluation of the reaction $ZnCaO_2$ nanocomposite (600°C) with 2-CEES at ambient temperature (25±1°C) via GC analysis shows that a high potential exists for degradation of 2-chloroethyl ethyl sulfide. Generally, with increasing the time, higher values sulfurous molecules have destructed. Thus, after 12 hours, 100% of 2-CEES molecules in contact with the $ZnCaO_2$ nanocomposite catalyst (in the n-pentane solvent) were destructed. The GC chromatograms and data's curve for the different times are shown in Figures 7, 8 and Table 2. After the reaction, the structure of nanocomposite was investigated via FTIR spectrum (Figure 9). The any new peaks in corresponded to adsorbed 2-CEES. Hence, 2-CEES molecules were destructed about perfectly. Thereafter, the reaction mixtures were analyzed by GC-MS (gas chromatography coupled with mass spectrometry) for the characterization of reaction products. Data illustrates the formation of two products by detector. One of the spectra has m/z values at 88, 71, 61, 47 and 27 thus indicating the formation of EVS and another one has the m/z values at 106, 89, 75, 61, 48 and 28, and indicates the formation of HEES thus emphasizing the role of elimination and hydrolysis reaction in the removal of 2-CEES (m/z values at 123, 109, 91, 75, 61, 47 and 28) thereby rendering it non-toxic (Figure 10).

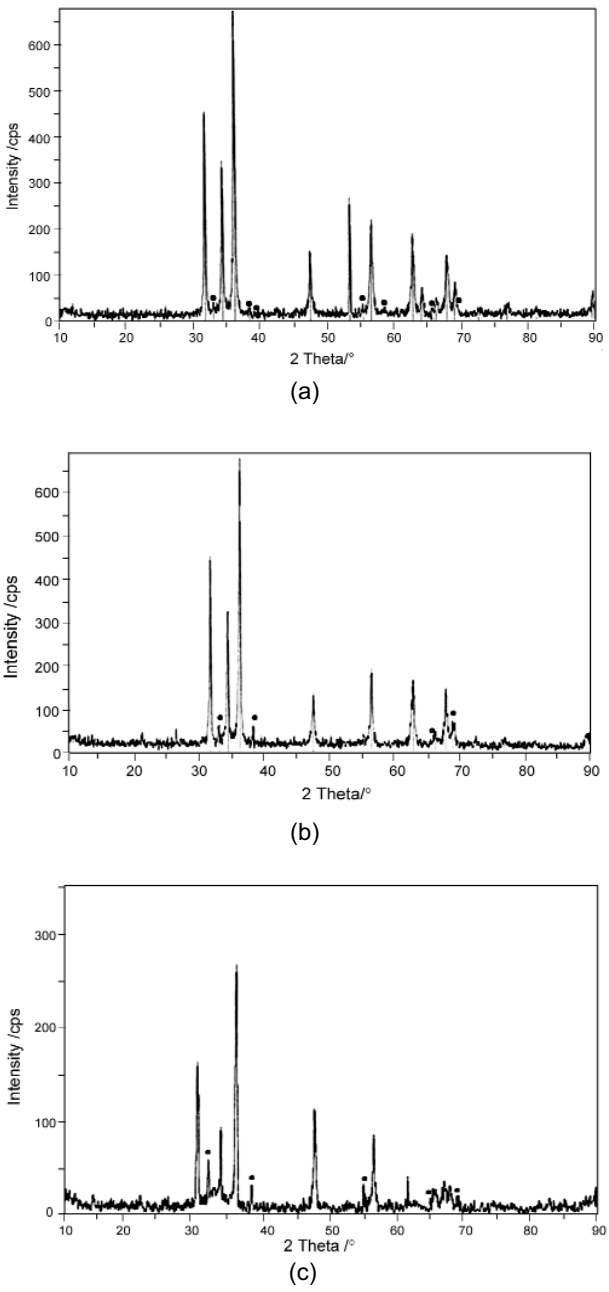


Figure 6: *XRD patterns of synthesized $ZnCaO_2$ nanocomposites at a) 500, b) 600 and c) 700°C.*

3.5. ^{31}PNMR and FT-IR studies

^{31}PNMR spectra and data's curve for interaction between $ZnCaO_2$ nanocomposite (600°C) and DMMP (dimethyl methyl phosphonate) in the presence of different times are shown in Figure 11, Tables 3 and 12, respectively. The chemical shift for DMMP H_3PO_4 were δ= 33 and 0 ppm, respectively. The intensity of the DMMP area under curve

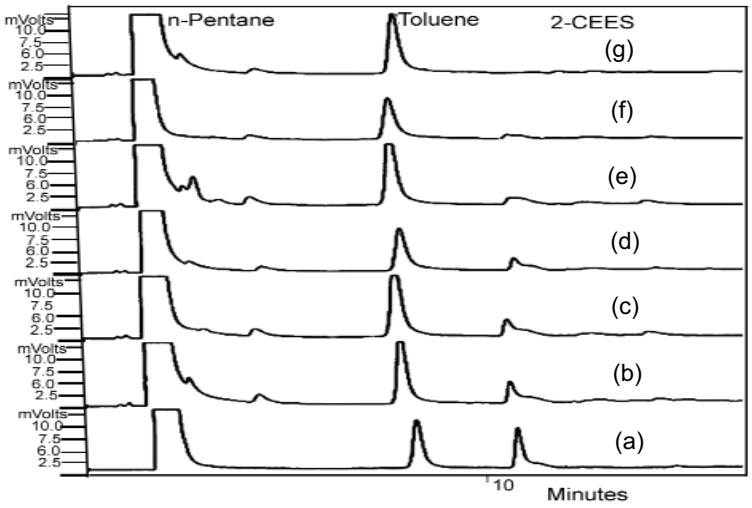


Figure 7: *GC chromatograms for 2-CEES on $ZnCaO_2$ nanocomposite.*

Table 2: *The results of GC analysis in the presence of different times and pentane solvent.*

Sample	Time(h)	Adsorbed and Destructed % by $ZnCaO_2$ nanocomposite
a	Blank(0)	100.00
b	2	82.25
c	4	64.43
d	6	56.67
e	8	25.15
f	10	8.60
g	12	00.00

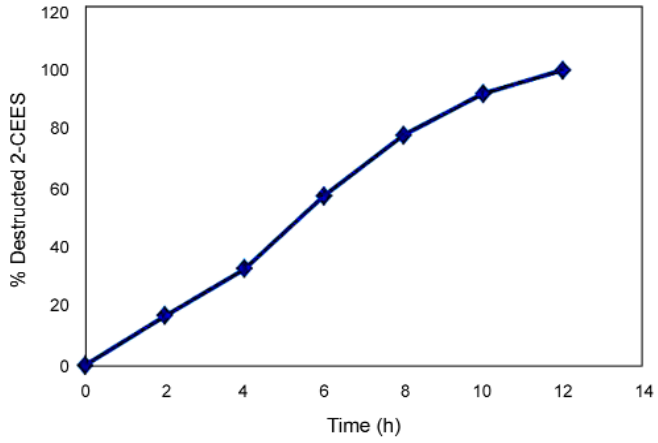


Figure 8: *The curve of destructed 2-CEES% versus time.*

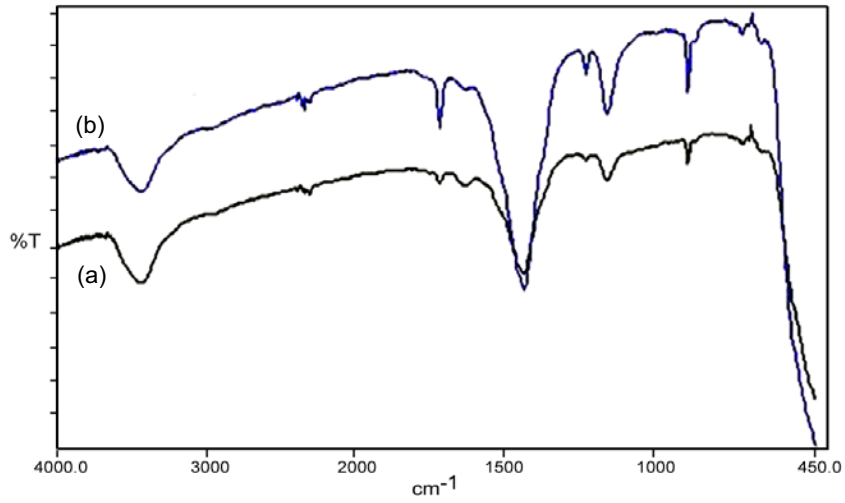


Figure 9: *FT-IR spectra of 2-CEES/$ZnCaO_2$ nanocomposite (600°C), a) before and b) after the reaction.*

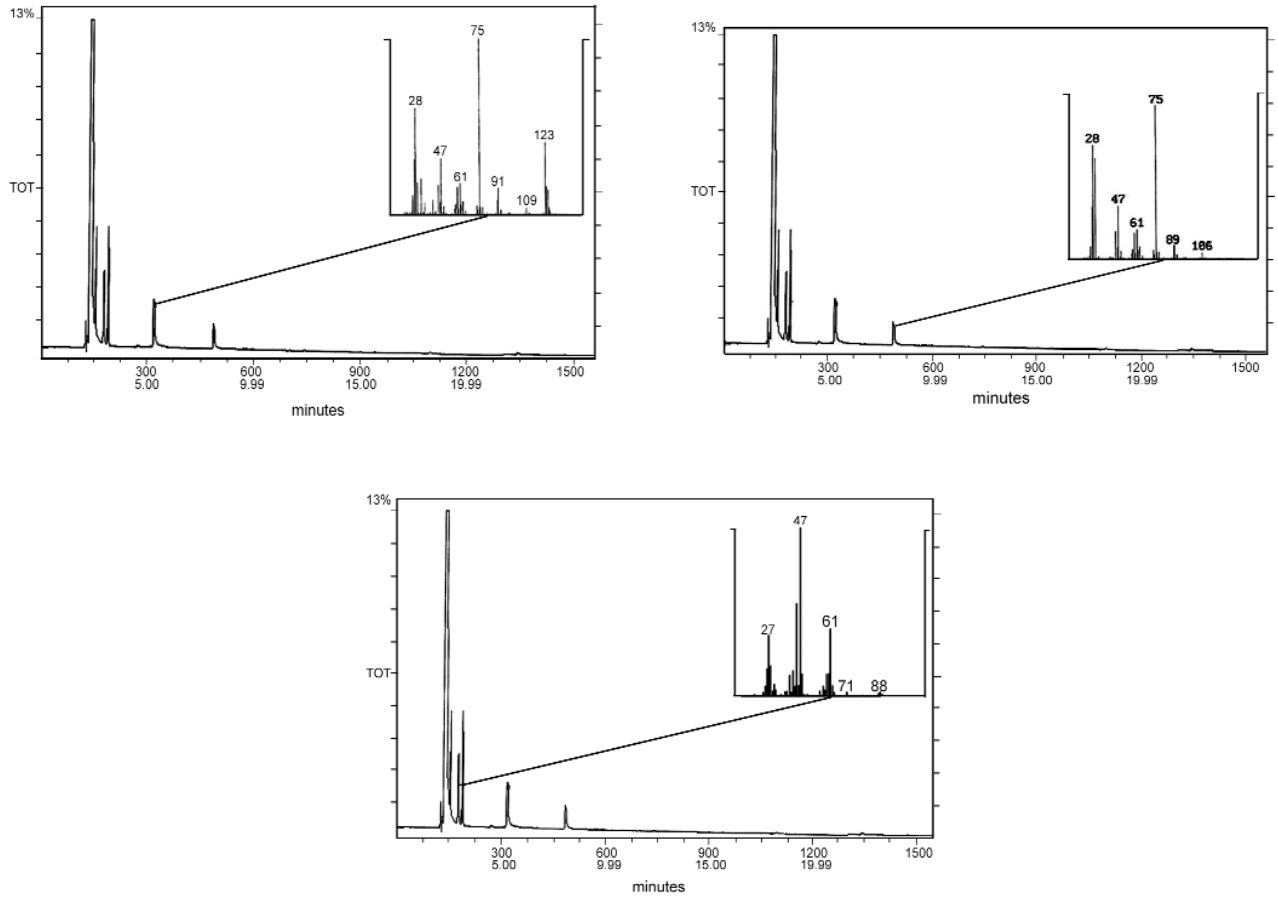


Figure 10: *GC-MS analysis results for reaction of 2-CEES/$ZnCaO_2$ nanocomposite and it's the destruction products.*

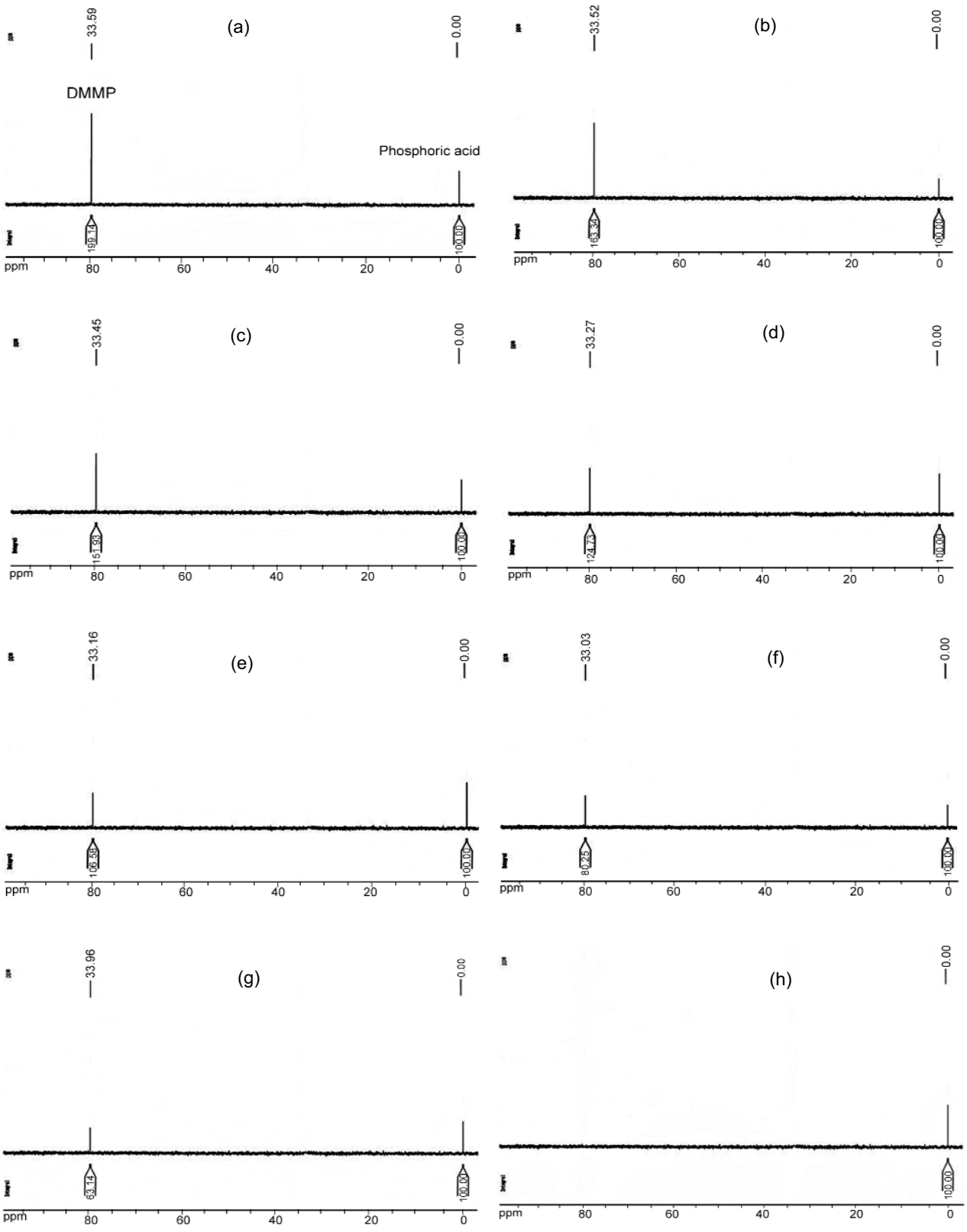


Figure 11: *^{31}PNMR spectra of the adsorption DMMP on the $ZnCaO_2$ nanocomposite at differernt times.*

Table 3: *The results of ^{31}PNMR spectra in the presence of different times.*

Sample	Time(h)	Concentration (DMMP) after reaction(Molar)	DMMP AUC / phosphoric acid blank AUC	% Adsorption(DMMP) by $ZnCaO_2$ nanocomposite
a	0(blank)	0.03	199.14	0
b	1	0.0246	163.34	17.98
c	2	0.0229	151.93	23.71
d	3	0.0188	124.73	37.37
e	4	0.0161	106.58	46.48
f	5	0.0121	80.25	59.70
g	6	0.0114	63.14	67.34
h	14	0	0	100

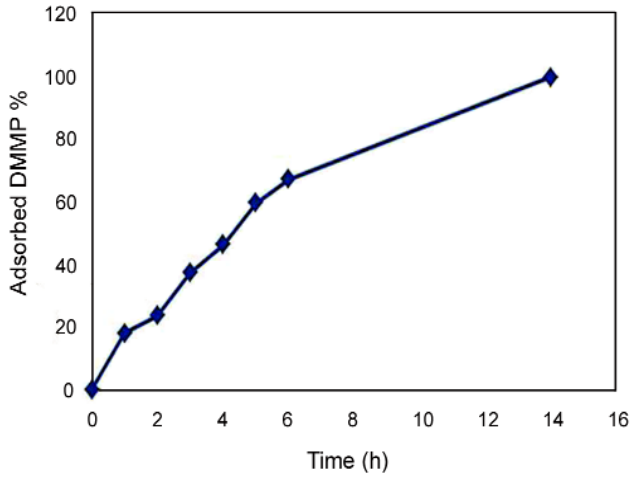


Figure 12: *The curve of adsorbed DMMP% versus time.*

(AUC) in comparison to AUC phosphoric acid blank and also concentration (DMMP) after reaction with increasing the time was decreasedbut, any new peak appears for the destruction product. Hence, we can say that after 14 h, 100% organo-phosphosphate molecule was adsorbed. After the reaction, the adsorption of DMMP on the nano-composite was investigated via FT-IR spectrum (Figure 13). The new peaks in 1186.05, 1066.04 and 3637.68 cm^{-1} are corresponded to adsorb DMMP. Hence, the structure of catalyst after the interaction was remained. After investigation of reactions 2-CEES and DMMP with $ZnCaO_2$ nanocomposite catalyst, that's proposed mechanisms in the presence of nanocomposite which are shown in Schemes 1 and 2. For the interaction between sulfurous compound and nanocomposite two sections were investigated. Section I) Adsorption reaction with nucleophillic attack the H atoms of composite to the chlorine and sulfur atoms of

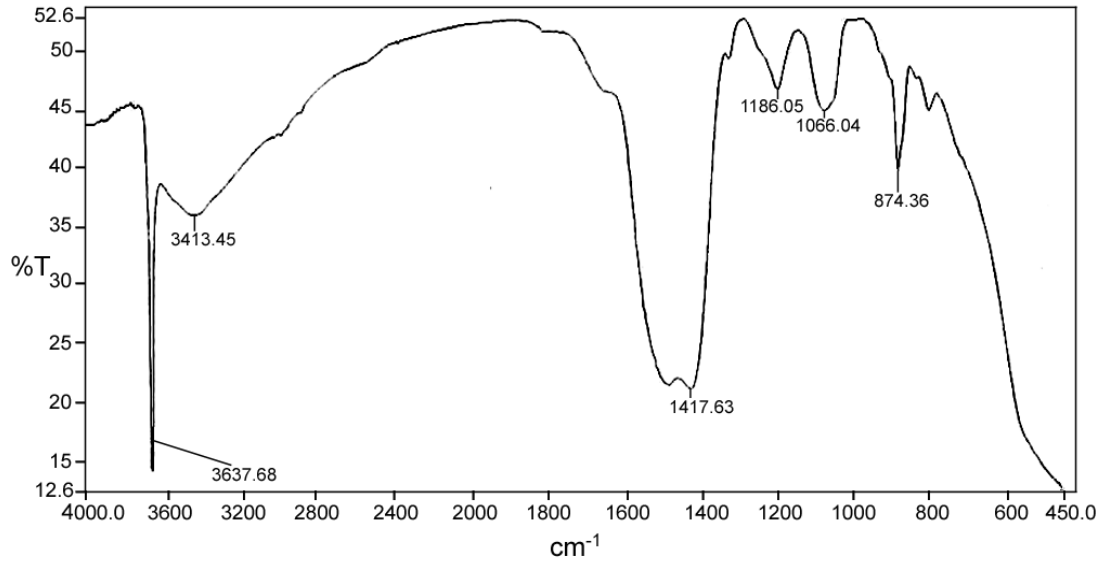
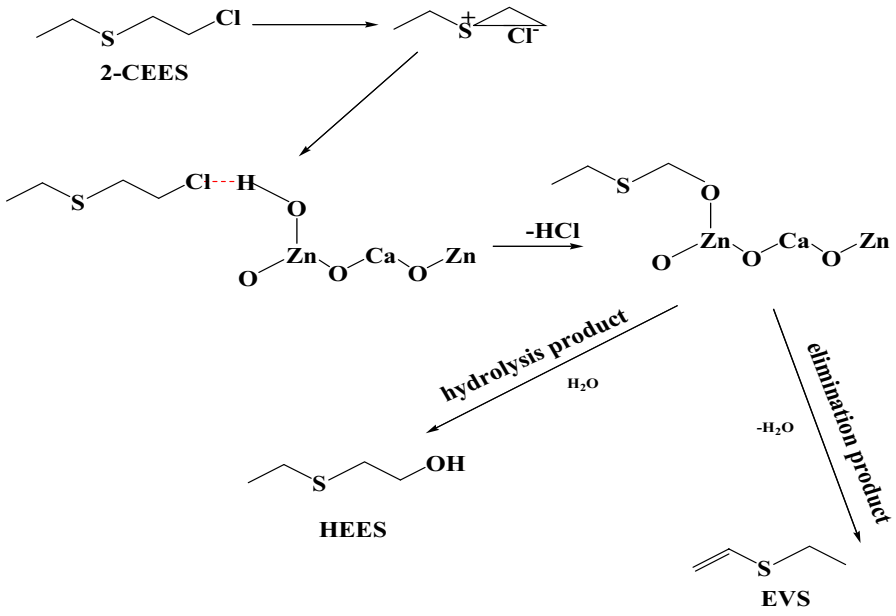
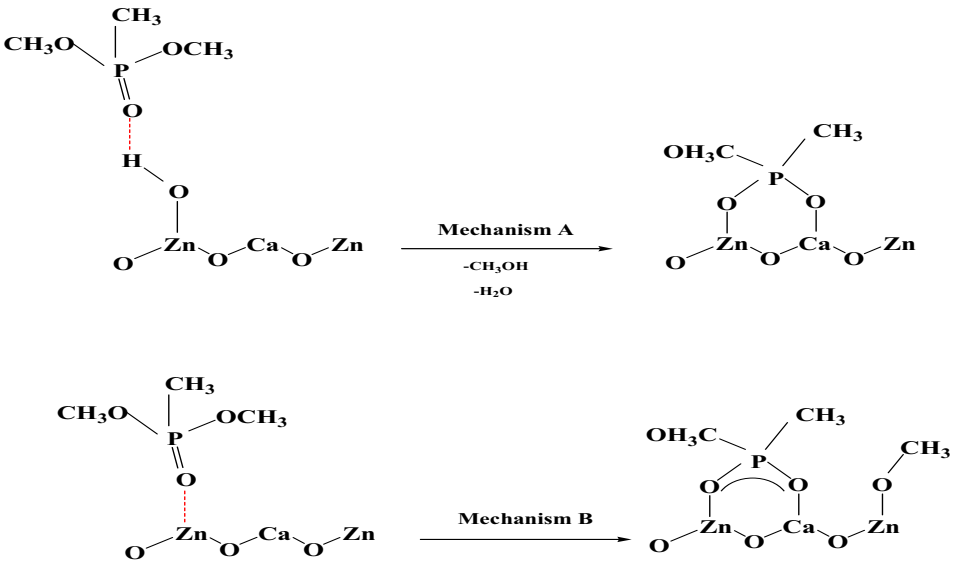


Figure 13: *FT-IR spectrum of the adsorption DMMP on the $ZnCaO_2$ nanocomposite.*



Scheme 1: *Proposed mechanism for the adsorption/destruction of 2-CEES on $ZnCaO_2$ nanocomposite catalyst.*

2-CEES molecule. In this interaction, the chlorine atom in 2-chloroethyl ethyl sulfide will be removed (the dehalogenation reaction). Section II) in the present and absence of H_2O molecule, the hydrolysis and elimination products were revealed, respectively. Also, in the interaction DMMP /$ZnCaO_2$ nanocomposite, two mechanisms were shown. In mechanism A: the bonding between oxygen atom of organo phosphorous compound and active sites of nanocomposite are produced. Then,



Scheme 2: *Proposed mechanisms for the adsorption of DMMP on $ZnCaO_2$ nanocomposite catalyst.*

by elimination of CH_3OH, DMMP on the catalyst was adsorbed. In mechanism B: the bonding between oxygen atom of organo phosphorous compound and Zn or Ca atoms of nanocomposite are produced that by elimination of CH_3OH and its adsorption on the catalyst any product was seen.

4. CONCLUSIONS

In summary, sulfurous and organo phosphorous compounds such as 2-CEES and DMMP are the ideal conditions for the adsorption/destruction of SCH_2CH_2Cl and P=O groups containing pollutants. The sol-gel pyrolysis method has been successfully used for synthesis of $ZnCaO_2$ nanocomposites at different temperatures (500-700°C) with to the hexagonal phase with wurtzite structure of zinc oxide and calcium oxide with FCC phase. This method is simple, environmentally friendly and low cost for production nanocomposite catalyst. The structure and the morphology of nanoparticles were investigated by XRD, SEM /EDAX and FT-IR techniques. The EDAX analysis for the synthesized nanocomposite (600°C) showed that CaO wt% and the average particles size was 2.05 wt% and 33 nm, respectively. In the other, synthesized nanocomposite (500 and 700°C), average particles size is higher. Thus, in this research, the best of temperature for the synthesized nanocomposite $ZnCaO_2$ is 600°C. The results obtained in this study demonstrate that $ZnCaO_2$ nanocomposite has a high catalyst potential for adsorption/destruction of 2-CEES and DMMP molecules that wereinvestigated via GC, GC-MS and ^{31}PNMR analyses, respectively. The 2-CEES and DMMP are absorbed about perfectly after 12 and 14 hours respectively and the destruction products of 2-CEES with nanocomposite; i.e. hydroxyl ethyl ethyl sulfide (HEES) and ethyl vinyl sulfide (EVS) were identified.

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