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A Novel Method for the Synthesis of CaO Nanoparticle for the Decomposition of Sulfurous Pollutant

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Abstract

In this research, CaO (calcium oxide) nanoparticles were synthesized by Co-Precipitation method in the absence and presence of Polyvinylpyrrolidone (PVP) via using calcium (II) nitrate. The Polyvinylpyrrolidone (PVP) was used as a capping agent to control the agglomeration of the nanoparticles. The synthesized samples were characterized via SEM, XRD and FTIR techniques. The average sizes of nanoparticles were determined by XRD data and Scherer equation. The decomposition reactions of 2-chloroethyl phenyl sulfide (2-CEPS) as a sulfurous pollutant has been investigated on the CaO nanoparticles (NPs)/Polyvinylpyrrolidone (PVP) surface at ambient temperature and monitored via using gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and FTIR spectrum. The GC analysis results revealed that 75% and 100% of 2-CEPS was found to be decomposed (adsorbed/destructed) in isopropanol and heptane solvents with weight ratio of 1:40(2-CEPS: CaO) after 12 h, respectively. On the other hand, these values for the weight ratios of 1:10, 1:20 and 1:30 were lower. The hydrolysis and elimination products; i.e. hydroxyl ethyl phenyl sulfide (HEPS) and phenyl vinyl sulfide (PVS) were identified by GC-MS respectively.

Keywords: *CaO (calcium oxide) nanoparticles, Co-Precipitation, Polyvinylpyrrolidone (PVP), 2-CEPS, Decomposition, Adsorbed/destructed.*

Introduction

The 2-chloroethyl phenyl sulfide (2-CEPS) is for the class of compounds containing sulfurous pollutant with the highly toxic that used such as pesticides, poses inevitable threat to persons who make contact; thereby causing

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health hazards [1-6]. The different methods are for decomposition and elimination of these compounds [7-9]. A series of materials including, bleach, potassium per sulfate, ozone, sodium per borate were used as active adsorbents along with surfactants in micro-emulsions for detoxification of pesticides [1]. Certain disadvantages exist with the use of these adsorbents such as environmental contaminates. In recent years, nanocrystalline inorganic metal oxides as solid reactive catalyst sorbents instead of liquid adsorption media were investigated [1014]. Strong adsorbs ability and enhanced reactivity towards the toxicants makes them the potential materials for the decomposition applications. These intriguing properties within the above materials are expected to be aroused owing to the high surface area due to smaller particle size and the reactive sites tailored in the form of edge and corner defects, unusual lattice planes, etc.

Most likely, these active sites react in a stoichiometric fashion, thereby rendering the adsorbed toxic agents to non-toxic ones and the reactions are analogous to their solution behavior. Recent investigations have explored the promising decomposition applications of nanosized metal oxides such as AP-MgO, AP-CuO, AP-Fe_2O_3, AP-Al_2O_3 and AP-CaO [15-20]. There are several methods for the synthesis of nanoscale CaO, including sol-gel[21], gas phase condensation[21], laser ablation[21], flame processing[22], sonochemical, microwave plasma[23], hydrothermal synthesis[24], electric dispersion reaction, combustion synthesis, spray pyrolysis, mechanochemical synthesis, reverse micelle and finally ultrasonic process[25-27]. A suitable process for synthesis of nanoparticles is using of Co-Precipitation method [28, 29]. To prevent increasing particle size, a polymer is often used, either natural or synthetic, with some affinity for metals.

The polymer is adsorbed on the cluster in aqueous solution and reduced surface tension. These substances also control both the reduction rate of metal ions and the agglomeration process of metal atoms. It was reported that polyvinyl pyrrolidone (PVP) could stabilize colloidal particles in water and many non-aqueous solvents by adsorbing onto a broad range of materials, such as metals (e.g., iron, silver and gold), and metal oxides (iron oxide, alumina and TiO_2) [30-32]. Calcium oxide (CaO) is an important inorganic compound which is used across various industries as catalyst, toxic-waste remediation agent, adsorbent, etc [33-36]. In the present work, the synthesis of CaO nanoparticles by Co-Precipitation in the absence and presence of Polyvinylpyrrolidone (PVP) as a capping agent was reported. Then, we have focused our attention on the CaO nanoparticles/Polyvinyl pyrrolidone (PVP) surface as a solid catalyst due to good catalytic properties and high performance for the decomposition of the 2-CEPS.

Experimental

Materials

$Ca(NO_3)_2.6H_2O$, sodium hydroxide, Polyvinyl pyrrolidone (PVP) are purchased from Merck Co. (Germany). Isopropanol, heptane, toluene, 2-CEPS (2-chloroethyl phenyl sulfide) form Sigma–Aldrich Co. (USA) were used as received.

Physical characterization

The morphology of the products was carried out using Field Emission Scanning Electron Microscope (SEM, LEO-1530VP). 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). Sample were scanned at 2°/min in the range of 2θ = 0110°. The IR spectrum was scanned using a Perkin-Elmer FTIR (Model 2000) in the wavelength range of 450 to 4000 cm^{-1} with KBr pellets method. GC and GC-MS (Varian Star 3400 CX, OV-101 CW HP 80/100 2m×1.8 in and DB 5 MS, 101 mic, 30m×0.25mm) instruments were used for the investigation interaction of 2-chloroethyl phenyl sulfide on the CaO nanoparticles surface. Temperature program for GC: 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 (held for 4 min) and 220 °C, to reach the final temperature (for 4 min); the temperature was increased at rate of 20 ^oC/ min for 13 min. Also, detector temperature was 230 ^oC.

Synthesis of CaO nanoparticles catalyst by Co-Precipitation method

An appropriate amount of $Ca(NO_3).6H_2O$ were dissolved in water and heated to 40 ^oC. While the solution was being stirred rapidly, 20 mL of NaOH 0.1M was added to the solution. After 30 minutes the reaction was halted; filtering and washing steps at pH=7 were carried-out. As a result the precursors of CaO; i.e. Ca $(OH)_2$ was produced which were left for 24 h at 60 ^oC ±10 0C to be dried. The dried precursors were calcinated at 300 ^oC for 2 h after which CaO powder was formed [32]. The ionic equation of the reaction is as followed (1):

$$6Ca^{2+}+12OH^{-}\rightarrow 6Ca(OH)_2\downarrow \rightarrow 6CaO+6H_2O \quad (1)$$

Co-Precipitation method in the presence of Polyvinyl pyrrolidone (PVP)

The procedure of this method is similar to the Co-Precipitation method. The difference is the acting of PVP as a capping agent to control the agglomeration of the nanoparticles [32].

Procedure reaction of the 2-CEPS with CaO nanoparticles

For this purpose, 10 μL of 2-CEPS, 5 mL of isopropanol or heptane as solvent and 10 μL of toluene as internal standard and 5, 50, 100 and 150 mg of CaO nanoparticles/Polyvinyl pyrrolidone (PVP) sample were added to the 50 mL Erlenmeyer flask, respectively. To do a complete reaction between catalyst and sulfurous compound, all samples were attached to a shaker and were shaken for about 12 h. Then, by micropipet extracted 10 μL of solutions and injected to GC and GC-MS instruments.

Result and discussion

SEM analysis

The SEM images of the CaO nanoparticles in the absence and presence of Polyvinylpyrrolidone (PVP) are shown in Figure 1. Analyzing the morphology aspect of the nanoparticles by studying the images indicates that the synthesized size nanoparticles are less than 100 nm. That means the synthesized catalysts have nano dimension. Also, the analysis results were emphasized that the smaller of the particle size is corresponded to the synthesized CaO nanoparticles with Polyvinyl pyrrolidone (PVP).

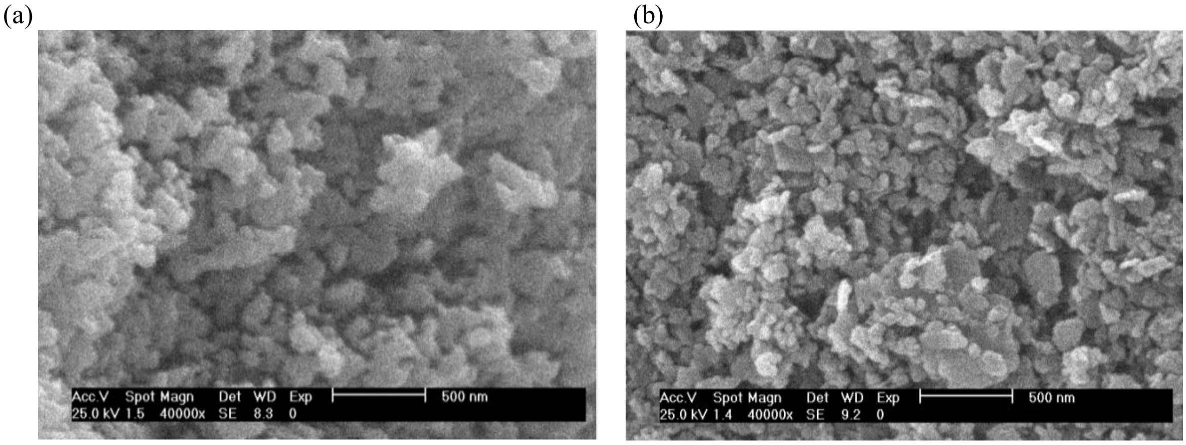


Figure 1. SEM images of CaO NPs in the, (a) absence and (b) presence of Polyvinyl pyrrolidone (PVP).

X-ray diffraction (XRD) study

The structure of prepared CaO nanoparticles/ Polyvinyl pyrrolidone (PVP) was investigated via X-ray diffraction (XRD) measurement (Figure 2). The average particle size of nanoparticles was investigated from line broadening of the peak at $2\theta=0110°$ via using Debye-Scherrer formula (1):

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

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 particles size by Debye-Scherrer formula was estimated to be 15 nm. The information obtained from XRD also confirms the above findings.

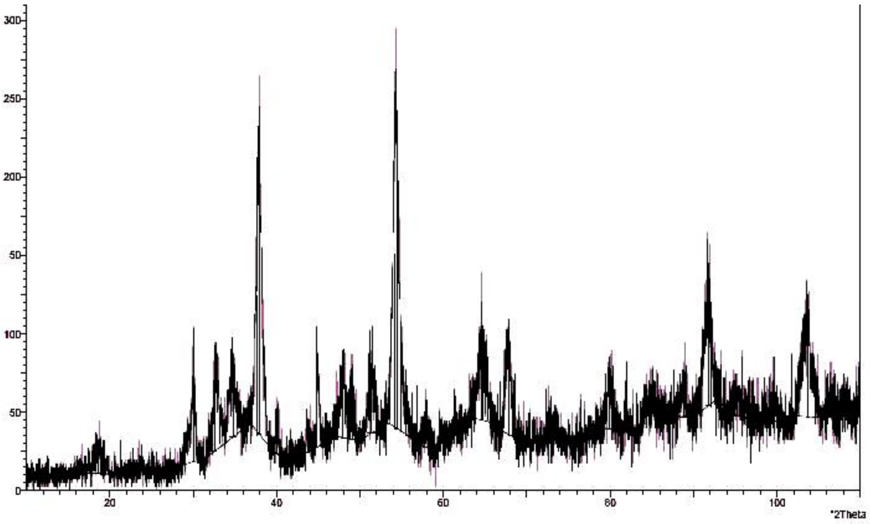


Figure 2. XRD pattern of synthesized CaO NPs/Polyvinyl pyrrolidone (PVP).

FTIR study

In Figure 3, FTIR spectrum of the CaO nanoparticles/Polyvinyl pyrrolidone (PVP) is shown. The peaks at 1632 and 1493 cm^{-1} are assigned to CO2 absorbed on the surface of nanoparticles. The peaks at 1350 and 898 cm^{-1} are assigned to C-H and C-C bonding vibrations of organic impure in the synthesized sample, respectively. The shoulder at 3429 cm^{-1} is present in the spectrum evidence of (O-H) stretching vibration. The strong absorbed peak around 450 cm^{-1} is corresponded to Ca−O bond. After the characterization, were used to study the decomposition reactions of 2-chloroethyl phenyl sulfide (2-CEPS) molecule on the CaO nanoparticles/Polyvinyl pyrrolidone (PVP) surface as a solid catalyst at ambient temperature.

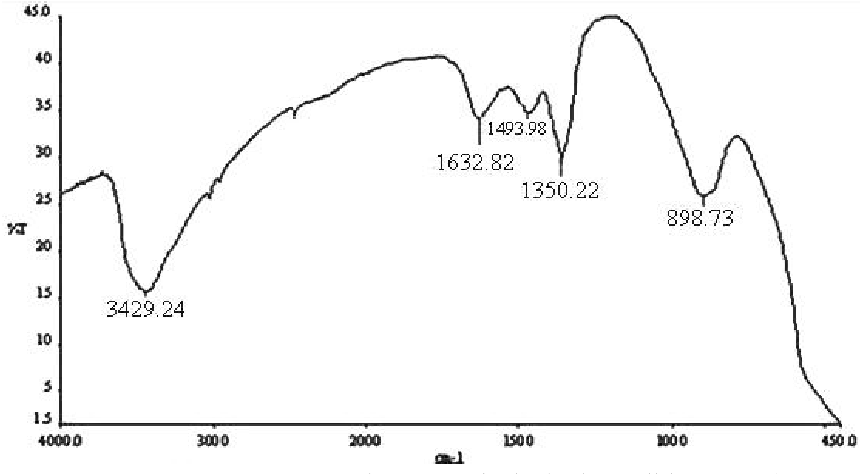


Figure 3. FTIR spectrum of CaO NPs/Polyvinylpyrrolidone (PVP).

GC analysis

For the evaluation of the reaction of 2-CEPS as a sulfurous pollutant on the CaO NPs/ Polyvinyl pyrrolidone (PVP) surface at ambient temperature GC analysis was selected. The effects of the weight ratio and solvent were investigated. Generally, with increasing the weight ratios, higher values of sulfurous molecules have adsorbed and destructed. In addition to this, the reaction is done very faster via using a solvent. The GC chromatograms and area under curve (AUC) data's are shown in Figures 4 and 5 and Tables 1 and 2. The isopropanol, heptane, toluene and 2-CEPS are diagnosed at a retention time 1.9, 3.5, 8.4 and 10.6, respectively. The surface ratio was determined by the AUC values of 2-CEPS to toluene as internal standard.The results illustrated that 75% and 100% of 2-CEPS in contact to the CaO NPs with weight ratio of 1:40 (2-CEPS: CaO) in isopropanol and heptane solvents were decomposed after 12 h, respectively. Other the weight ratios of 1:10, 1:20 and 1:30 have the lower values. However, that polar solvent hinders the reaction, even though polar reaction transition state must be involved. These data indicate the polar solvents can compete with reactive site on the CaO surface including Bronsted acid and Lewis acid sites. In particular the blocking of Lewis acid site would hinder the coordination of the 2-CEPS. Since isopropanol is such a strong hindrance to the reaction, this tends to lend further support to the idea that isopropanol simply blocks access to the sorbent surface.

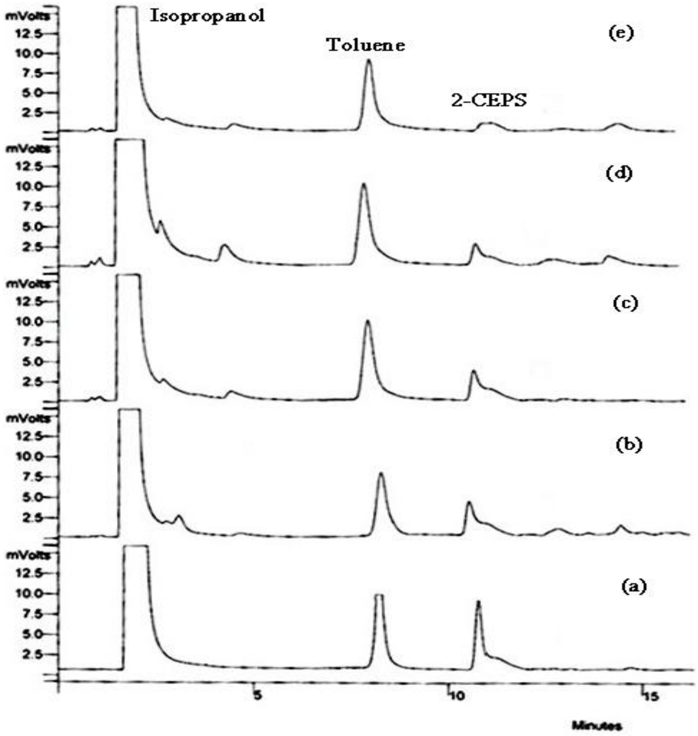


Figure 4. GC chromatograms of 2-CEPS on CaO NPs/Polyvinylpyrrolidone (PVP) in isopropanol.

Table1. The results of GC chromatograms in the presence of different weight ratios and isopropanol solvent.

sample	Ratio	AUC/Toluene(1)	AUC/2-CEPS(2)	Surface ratio(AUC 2/ AUC 1)	Surface ratio% or % decompose
A	Blank	294585	273375	0.9280	100
B	1:10	280617	237935	0.8479	91.37
C	1:20	350069	246553	0.7043	75.90
D	1:30	369095	203112	0.5503	59.31
E	1:40	350456	80359	0.2293	24.71

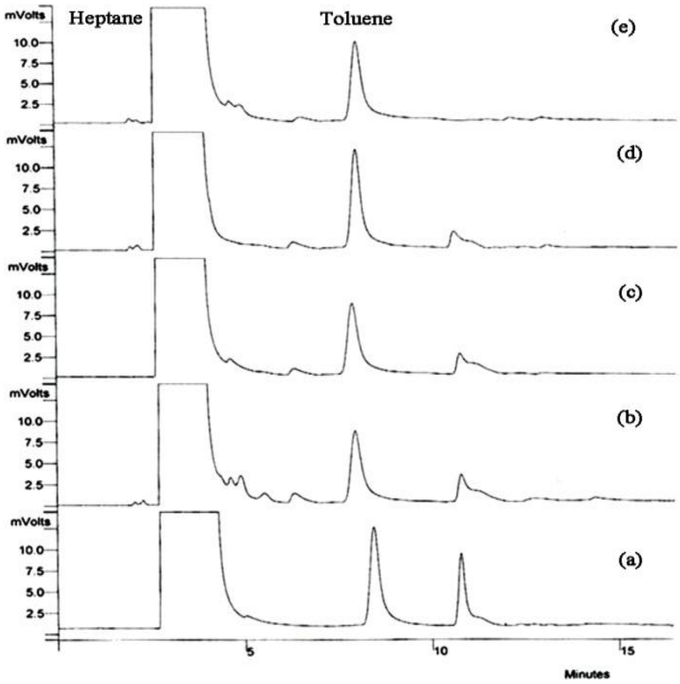


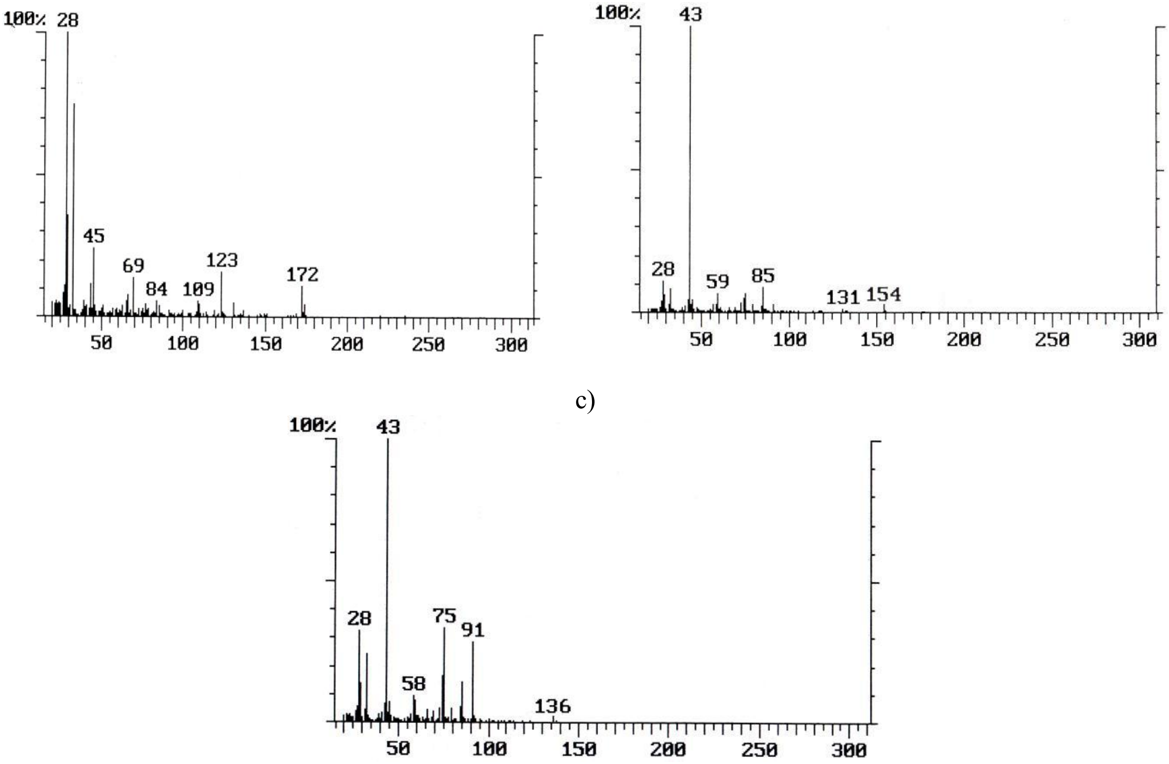
Figure 5. GC chromatograms of 2-CEPS on CaO NPs/Polyvinylpyrrolidone (PVP) in heptanes.

Table2. The results of GC chromatograms in the presence of different weight ratios and heptane solvent.

Sample	Ratio	AUC/Toluene(1)	AUC/2-CEPS(2)	Surface ratio(AUC 2/ AUC 1)	Surface ratio% or % decompose
A	Blank	453933	260693	0.5744	100.00
B	1:10	334852	162891	0.4864	84.69
C	1:20	342651	121791	0.3554	61.88
D	1:30	434328	83649	0.1925	33.53
E	1:40	428017	0	0	00.00

GC-MS analysis

To identify the composition of quantify destruction products of CaO NPs/Polyvinyl pyrrolidone (PVP) exposed to 2-CEPS gas chromatography coupled with mass spectrometry (GC-MS) analysis was used. The detector was set to scan a mass range of m/z values at 28 to 172 for 2-chloroethyl phenyl sulfide (2-CEPS), 28 to 154 and 28 to 136 for hydroxyl ethyl phenyl sulfide (HEPS) and phenyl vinyl sulfide (PVS), respectively. In Figure 6, GC-MS analysis and failures of the mass spectra for 2-CEPS, HEPS and PVS are shown. These compounds have a lower toxicity in comparison with 2-CEPS.



c)

Figure 6. GC-MS analysis and failures of the mass spectra: a) 2-CEPS, b) HEPS and c) PVS.

FTIR spectrum

After the reaction, the structure of CaO NPs/ Polyvinylpyrrolidone (PVP) was monitored by FTIR spectrum (Figure 7). The any new peaks were seen in corresponded to adsorb of 2-CEPS. Therefore, it can be concluded that 2-CEPS molecule was destructed perfectly.

After investigation of reactions between 2-CEPS and CaO NPs catalyst, that's proposed mechanism in the presence of nanoparticles which are shown in Scheme 1. For the reactions between sulfurous compound and catalyst two ways were investigated. I) The adsorption reaction with nucleophillic attack the H atoms of hydroxyl groups (Bronsted acid sites) of nanoparticles to the chlorine and sulfur atoms of 2-CEPS molecule (initially, cyclic sulfonium ion seem to be formed which being in non-volatile form of salt could not be extracted out and detected via GC). In this reaction, the chlorine atom in 2-chloroethyl phenyl sulfide will be removed (the dehalogenation reaction). II) In the present and absence of H_2O molecule, the hydrolysis and elimination products on the Lewis acid sites were revealed, respectively.

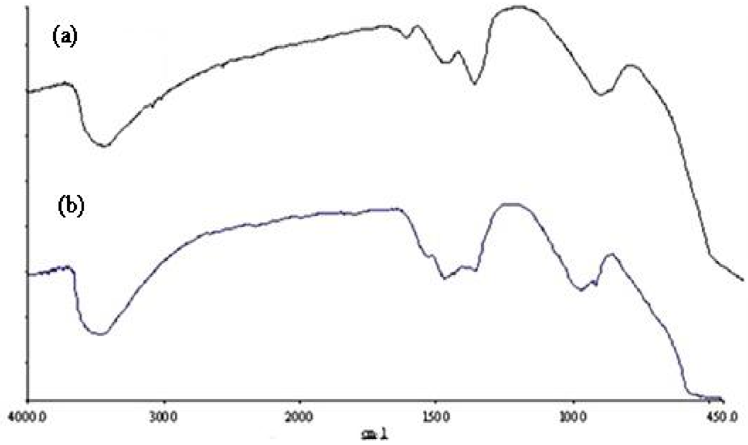
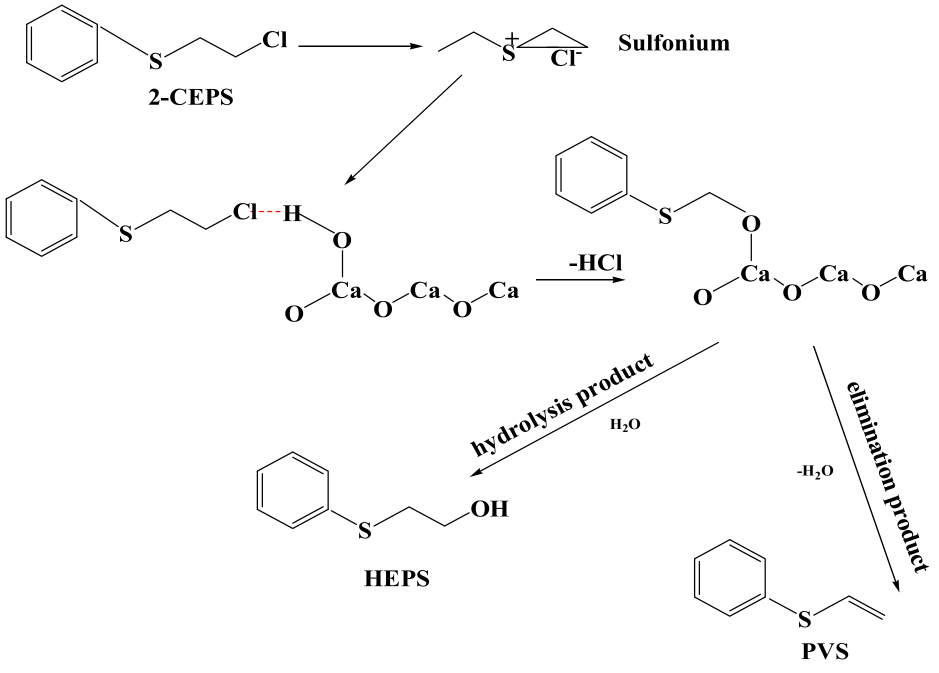


Figure 7. FTIR spectra of CaO NPs/Polyvinylpyrrolidone (PVP): a) before and b) after the reaction with 2-CEPS.



Scheme1. Proposed mechanism for the decomposition (adsorption/destruction) of 2-CEPS on the CaO NPs catalyst.

Conclusion

CaO nanoparticles (NPs) were synthesized by Co-Precipitation method in the absence and presence of Polyvinylpyrrolidone (PVP) and then characterized. Thereafter, CaO NPs/ Polyvinylpyrrolidone (PVP) was used for studying the decomposition reactions with 2-CEPS. The results obtained in this study demonstrate that CaO nanoparticles have a high catalyst potential for the adsorption/ destruction of 2-CEPS molecules that were investigated via GC, GC-MS and FTIR analyses, respectively. 75% and 100% of 2-CEPS in the isopropanol and heptane solvents with weight ratio of 1:40 was absorbed/destructed after 12, respectively and the destruction nontoxic products of 2-CEPS with nanoparticles; i.e. hydroxyl ethyl phenyl sulfide (HEPS) and phenyl vinyl sulfide (PVS) were identified.

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