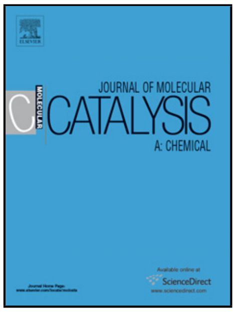

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Magnetic Fe_3O_4@MgAl–LDH composite grafted with cobalt phthalocyanine as an efficient heterogeneous catalyst for the oxidation of mercaptans

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Highlights

► ► Magnetically separable layered double hydroxide composite ► Heterogeneous cobalt phthalocyanine catalyst for oxidation of mercaptans under alkali free conditions ► Facile recovery of the catalyst by using external magnet and efficient recycling without change in catalytic activity ► Efficient conversion and higher product yields ► Improved methodology for sweetening of petroleum products

Graphical abstract

Abstract

Magnetically separable layered double hydroxide MgAl–LDH@Fe_3O_4 composite supported cobalt phthalocyanine catalyst was synthesized and used for the aerobic oxidation of mercaptans to corresponding disulfides under alkali free conditions. The catalyst exhibited excellent activity for the oxidation of mercaptans using molecular oxygen as an oxidant which can be effectively recovered by using an external magnetic field. In addition the covalent immobilization of cobalt phthalocyanine to MgAl–LDH@Fe_3O_4 support prevents the leaching of the catalyst and improves its activity and stability.

Keywords: Sweetening, Oxidation, Cobalt phthalocyanine, Immobilized catalys, Magnetically separable catalyst

1. Introduction

Presence of mercaptans (RSH), in the petroleum products are undesirable due to their foul odor and corrosive nature [1-4]. Therefore, removal of these mercaptans from refinery streams is necessary before end use. The process of removing mercaptans or converting these to less deleterious disulphides by catalytic oxidation is known as “sweetening”[5-6]. Sweetening involves the catalytic oxidation of the mercaptans to innocuous disulfides with air by cobalt phthalocyanines in the presence of caustic soda as a co-catalyst [7-10]. However, the use of caustic is undesirable due to its hazardous nature and its disposal issues due to the stringent environmental regulations[11]. Further, homogeneous nature of the catalyst makes this process less attractive due to difficulty in recovery and re-cyclability of the catalyst. One of the logical approaches to overcome both the limitations is the use of solid bases as support to immobilize homogeneous cobalt phthalocyanine catalyst which not only make the process caustic free but also make the catalyst easily recoverable and re-cyclable [12-17]. In this regard, Liu et al reported bifunctional catalysts composed of tetrasodium salt of cobalt(II)-tetrasulfophthalocyanine ($Co(II)Pc(SO_3Na)_4$, designated as CoPcTs) supported on different Mg–Al mixed oxides for the alkali free oxidation of mercaptans[18]. Recently, the nanosized support materials i.e. nanoparticles owing to their large surface area have emerged as efficient alternatives for the immobilization of homogeneous metal catalysts[19-22]. However, as the size of the particles is decreased, separation of the catalyst via filtration or centrifugation becomes a difficult and time-consuming procedure. The most appealing way to overcome this limitation is to catalyst with magnetic properties, allowing easy separation of the catalyst by simply applying an external magnetic field. Besides to the facile separation of the catalyst by external magnetic field, the magnetic nanocomposite matrices act as the stabilizer of the nanoparticles and thus providing a means to prevent aggregation[23-26]. Recently, magnetic composites have shown tremendous interest and widely been used for various applications including as photocatalysts for degradation of pollutants, water splitting for hydrogen production, and selective organic transformations[27-32]. In a recent report Mi et al reported the novel magnetic mixed metal Mg-Al layered double hydroxides (MgAl-LDH) supported gold nanoparticles for the oxidation of selective oxidation of alcohols[33].

In continuation to our ongoing effort for developing improved process for sweetening of etroleum products, herein we report novel magnetically separable MgAl–LDH@Fe_3O_4 (layered double hydroxide) composite covalently anchored with cobalt phthalocyanine for the oxidation of mercaptans using molecular oxygen as an oxidant under alkali free conditions. The catalyst showed excellent catalytic activity along with the facile recovery using an external magnetic field. After completion of the reaction, the catalyst was readily separated by using external magnet and reused for several runs without any significant loss in catalytic activity.

2. Experimental

2.1. Catalyst preparation

Iron(II) chloride (99.5%), iron(III) chloride (98%), mercaptans, cobalt phthalocyanine 98%, were purchased from Sigma-Aldrich. Cobalt phthalocyanine tetrasulfonic acid (CoPcS) was synthesized by treating CoPc with chlorosulphonic acid as following the literature procedure. All reagents were used without further purification. Deionized water was used in all experiments.

2.1.1 Synthesis Synthesis of iron magnetic nanoparticles (MNP) [34]

Fine sized magnetic nanoparticles were synthesized by precipitation method using ferrous chloride and ferric chloride in alkaline aqueous medium according to the literature procedure. In briefly, 5.2 g $FeCl_3$ (32 mmol) and 2.0g $FeCl_2$ (15.74 mmol) were dissolved in 25ml deoxygenated water containing 0.85 mL of 12.1 N HCl solution. The obtained solution was added drop-wise to 250 mL, 1.5 M NaOH with vigorous stirring to getting iron nanoparticles. The resulting MNPs were separated by using the external magnet and centrifugation washed with water and finally with 0.01 M HCl (500 mL).

2.1.2 Preparation of MgAl-LDH@MNP

In a 100 mL methanol/water (1/1) solution 0.104g MNPs were dispersed with the help of ultrasonication for 15 min. To this suspension an alkaline solution containing 1.280 g Na_2CO_3 and 1.600 g NaOH in 100 mL methanol/water (1/1) was added drop wise to get the pH=10. Then, another solution containing 2.31 g $Mg(NO_3)_2 \cdot 6H_2O$ and 1.12 g $Al(NO_3)_3 \cdot 9H_2O$ in 100 ml methanol/water(1/1) solution was added drop wise into the above suspension under vigorous stirring at constant pH 10 maintained by simultaneous addition of alkaline solution. The obtained gel was kept at 60 °C for 24 h. final product was isolated by decanting and washed with water five times and dried at 60 °C for 24h.

2.1.3 Immobilization of tetrasulfonated cobalt phthalocyanine (CoPcS) to MgAl-LDH@MNP

In a typical synthesis, 0.25 g CoPcS and 2 g MgAl-LDH@MNP were added to a round bottomed flask containing 100 mL ethanol/water (1/1) mixture and stirred for 24 hours at 80 °C. The synthesized heterogeneous material was thoroughly washed with ethanol, water and then dried at 60 °C for 24 h. Cobalt content as determined by ICP-AES was found to be 1.4 wt % (0.23mmol/g catalyst).

2.2 Catalyst characterization

Rough structural morphologies of materials were determined by using Scanning electron microscopy on Jeol Model JSM-6340F. While fine structure of samples was determine by High Resolution Transmission Electron Microscopy using FEI-TecnaiG^2 Twin TEM working at an acceleration voltage of 200 kV. For TEM analysis well dispersed aqueous samples were deposited on carbon coated copper grid. Phase structure and crystalline nature of samples were determined by XRD using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K_α radiation (λ= 1.5418 nm). FTIR spectra of samples were recorded on Perkin–Elmer spectrum RX-1 IR spectrophotometer. UV-visible light absorption pattern of materials were executed on Perkin Elmer lambda-19 UV-VIS-NIR spectrophotometer by using $BaSO_4$ as reference material. Thermal degradation pattern of LDH@MNP and CoPcS@LDH@MNP was calculated by thermo gravimetric analysis with the help of a thermal analyzer TA-SDT Q-600 in the temperature range 40 to 900 °C with heating rate was 10 °C/min under nitrogen flow. Brauner Emmett Teller (BET) surface area, pore volume, pore diameter and other surface properties of samples were obtained on Micromeritics ASAP2010 working in liquid nitrogen at 77 K. Inductively coupled plasma was used for the determination of cobalt content and was carried out by using inductively coupled plasma atomic emission spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc, USA). For ICP-AES samples were prepared by digesting 0.05 g catalyst with conc. HNO_3 and heated at 70 °C for 30 min and volume was making up to 10ml by adding de-ionized water. The yield of product was determined by GC-MS. Mercaptan contents of blended kerosene were determined by Mettler Toledo DL50 Rondolino potentiometer using a platinum counter electrode.

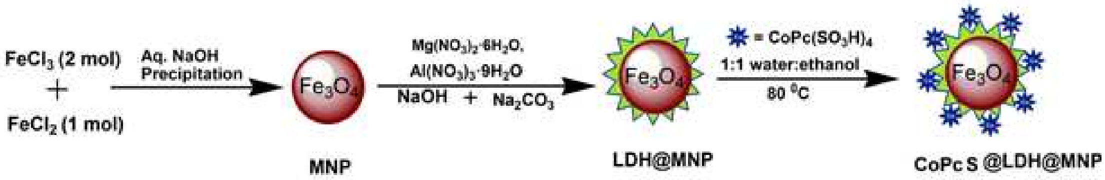
2.3 General experimental procedure for oxidation of mercaptans

Water (10 mL) and heterogeneous catalyst (0.12 g) and mercaptan (10 mmol) were charged in a 100 mL round bottomed flask. The obtained reaction mixture was heated at 70 ^{o}C in the presence of molecular oxygen under stirring. The reaction progress was monitored by collecting the samples in half-an-hour interval, extracted with diethyl ether and analyzed by GC-MS. In order to check the potential of developed catalytic system for sweetening of petroleum products, the kerosene oil was blended with n-dodecane mercaptan (300 ppm). The resulting sample was subjected for oxidation under optimized experimental conditions. The samples were withdrawn at various time periods and unreacted mercaptan content was determined by using a potentiostat having a platinum counter electrode. For comparison blank reactions were also carried out by using MgAl-LDH@MNP without CoPcS.

3. Results and discussion

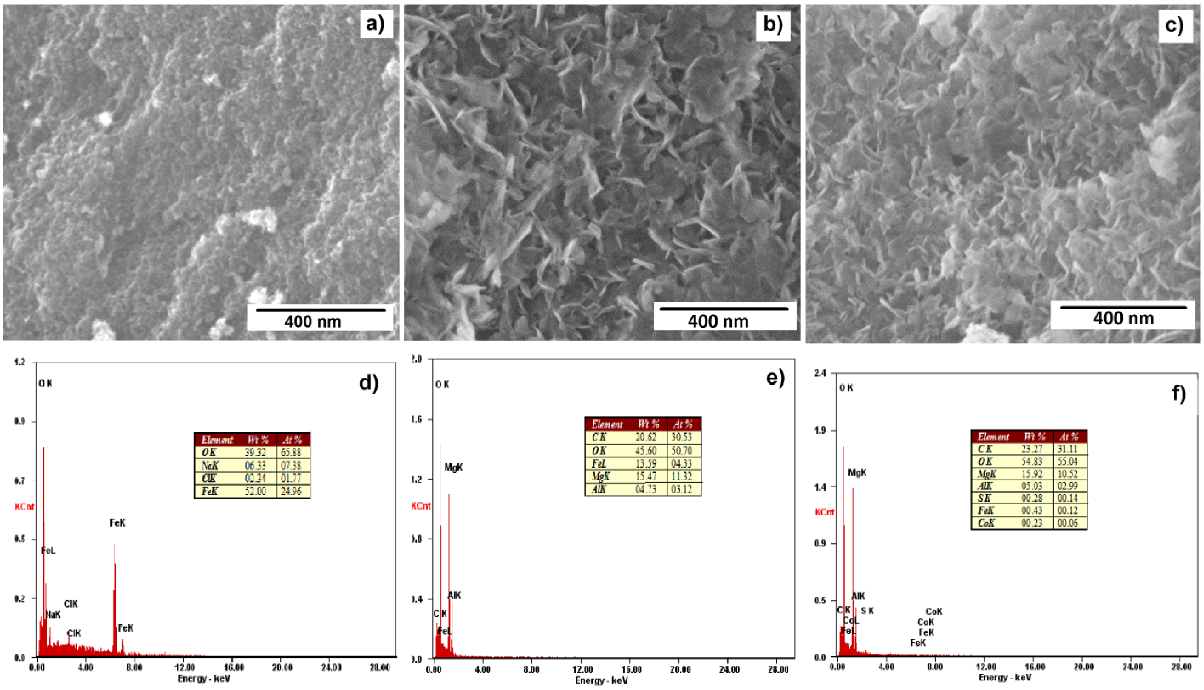
3.1 Synthesis and characterization of catalyst

At first Fe_3O_4 magnetic naoparticles were synthesized and subsequently coated with LDH by a simple co-precipitation method as suggested in the literature. In a typical synthesis, solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ in water/ethanol was precipitated in suspension of iron nanoparticles with maintaining pH 10 by adding Na_2CO_3 and NaOH solution simultaneously. The obtained gel was aged for 24h at 60 ^{o}C to facilitate the growth of LDH platelets on Fe_3O_4 nanoparticles. Finally CoPcS was immobilized to the synthesized MgAl-LDH@MNP (denoted as LDH@MNP) by intercalation of CoPcS molecules between LDH interlayers (Scheme 1). The cobalt content as determined by ICP-AES was found to be 1.4 wt % (0.23mmol/g catalyst).



Scheme 1: Synthesis of CoPcS@LDH@MNP catalyst

The rough microstructure of Fe_3O_4 magnetic nanoparticles, LDH@MNP and CoPcS@LDH@MNP was explored with the help of scanning electron microscopy. SEM image of MNP shows that very small sized particles around 15 nm to 20 nm were formed (Fig. 1). After the coating of LDH on MNP the honey comb type morphology of composite revealed the formation of efficient interlaced platelets. In case of CoPcS@LDH@MNP, the morphology remained almost intact, suggesting that the attachment of complex molecules did not change the surface morphology. As shown in EDX pattern, the weight percentage of iron in MNP was found to be 52.00 wt %, which subsequently decreased to 13.59 % after the coating of LDH. The remarkable decrease in the iron content of LDH@MNP confirmed the good coating of LDH on MNP's. The appearance of cobalt in EDX pattern of CoPcS@LDH@MNP revealed the presence of cobalt phthalocyanine in composite.



Element	Wt %	At %
O K	39.32	65.88
NaK	06.33	07.38
ClK	02.34	01.77
FeK	52.00	24.96

Element	Wt %	At %
C K	20.62	30.53
O K	45.60	50.70
FeL	13.59	04.33
MgK	15.47	11.32
AlK	04.73	03.12

Element	Wt %	At %
C K	23.27	31.11
O K	54.83	55.04
MgK	15.92	10.52
AlK	05.03	02.99
S K	00.28	00.14
FeK	00.43	00.12
CoK	00.23	00.06

Fig. 1: SEM image of a) MNP b) LDH@MNP and c) CoPcS@MNP, EDX pattern of d) MNP e) LDH@MNP and d) CoPcS@LDH@MNP

TEM images clearly showed that particles of Fe_3O_4 were coated with LDH and were of in the range of 15-20 nm. The ridge like structures in the TEM image of LDH@MNP was confirming the LDH coating on MNPs. After the attachment of CoPcS to the LDH@MNP the morphology remained almost similar, this was assumed due to the attachment of the CoPcS units on the LDH support.

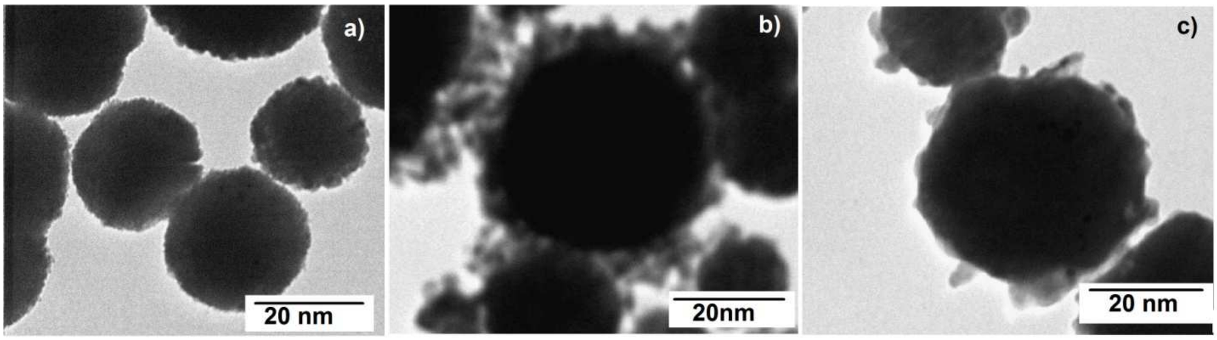


Fig. 2: TEM image of a) MNP b) LDH@MNP and c) CoPcS@LDH@MNP

The X-ray diffraction pattern of MNP, LDH@MNP and CoPcS@LDH@MNP is shown in Fig. 3. Magnetic nanoparticles exhibited very diffuse peaks corresponding to Fe_3O_4 at 2θ = 35.4°, 43.6°, 57.4° and 63.2° due to 311, 400, 511, and 440 plane reflections (JCPDS Card No. 65-3107) [35]. The peak intensity was found to be low because of very small size of nanoparticles. LDH@MNP gave sharp peaks at 2θ value 11.4°, 22.8°, 34.7°, 60.5° and 61.8° respectively due to 003, 006, 009, 110, and 113 plane of LDH [36-38]. No peaks of MNP's were observable because of higher coating of LDH and small size of MNP's. In analogy to the existing literature reports [39-40], the XRD pattern of magnetic LDH containing tetrasulfonated cobalt phthalocyanine was found to be identical with the precursor magnetic LDH (Fig. 3). Thus we presume that the phthalocyanine complex was attached on the surface of magnetic LDH via SO3- ions of CoPcS and not intercalated between the LDH layers by the ion-exchanged with carbonate anions in the LDH.

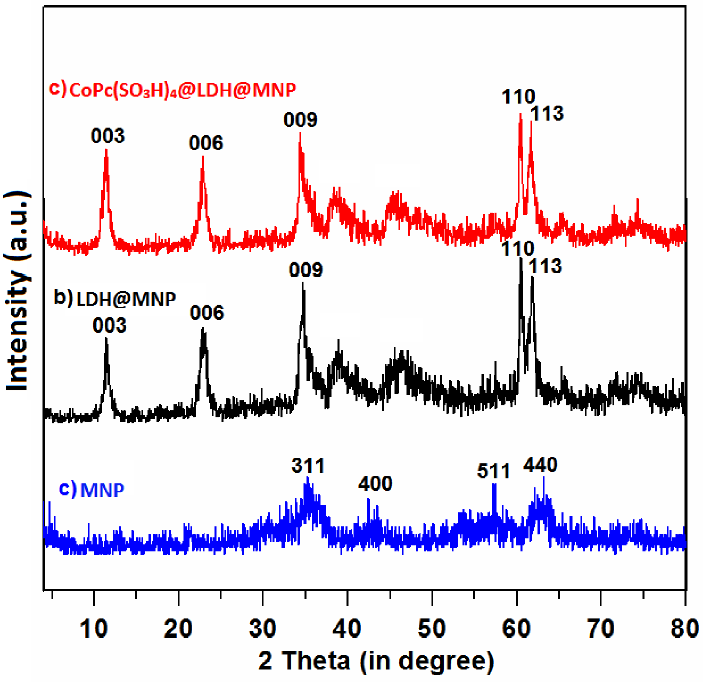


Fig 3: XRD of a) Iron MNP b) LDH@MNP and c) CoPc(SO_3H)$_4$@LDH@MNP

BET surface area, pore diameter and pore volume of synthesized materials was measured with the help of nitrogen adsorption desorption isotherm at 77 K. For LDH@MNP and CoPcS@LDH@MNP the adsorption desorption isotherm was Type IV which according to IUPAC recommendation suggested that the synthesized material was mesoporous in nature Fig. S1a [41]. The specific BET surface area (S_{BET}), mean pore diameter, and mean pore volume of LDH@MNP was found 93.40 m^2/g, 2.41 nm, and 0.28 cm^3/g respectively Fig. S1b. Whether for CoPcS@LDH@MNP these values were found to be 80.67 m^2/g, 5.29 nm, and 0.20 cm^3/g respectively. The surface area of magnetic LDH containing CoPcS did not significantly decreased after the attachment of CoPcS complex units to the magnetic LDH. This further confirmed that the CoPcS complex units were attached to the surface of LDH and were not intercalated between the LDH layers.

The UV-Vis absorption spectra of CoPcS exhibited two characteristic absorption band at

305 nm (Soret band) and 660 nm (Q band) respectively due to π→π* macrocycle ring transition Fig. 4a [42]. LDH@MNP gave a strong absorption band at 310 nm [43] that after the immobilization of CoPcS got slightly red shifted and Q band due to presence of CoPcS was also observed at 665 nm. These changes in the UV-Vis spectra clearly indicated the attachment of CoPcS complex to LDH@MNP.

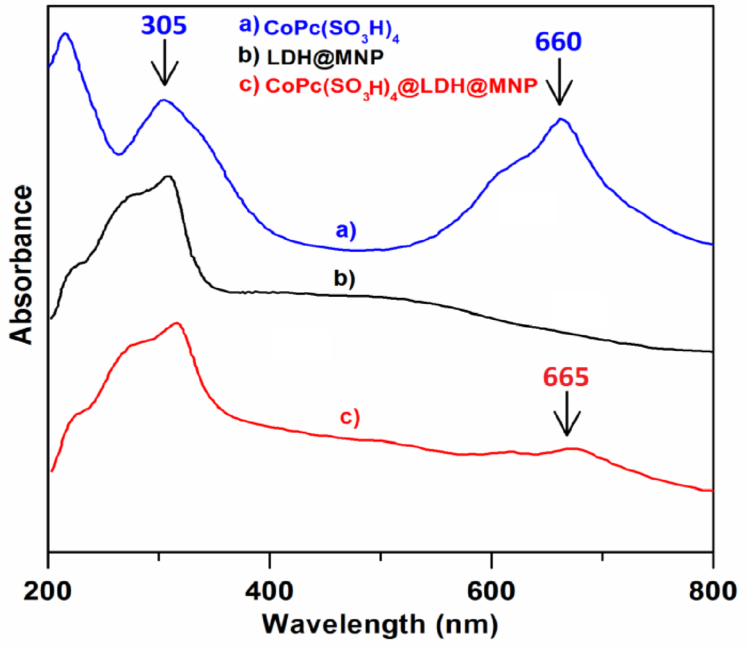


Fig 4: UV-Visible spectra of a) CoPc(SO_3H)$_4$ b) LDH@MNP c) CoPcS@LDH@MNP

Vibrational spectra of CoPcS Fig 5a showed characteristics ring vibrations at 572 cm^{-1}, 640 cm^{-1}, 750 cm^{-1}. The peaks at 923 cm^{-1}, 1110 cm^{-1}, and 1159 cm^{-1} were due to aromatic ring vibrations, C-H bending vibrations, C=N vibration and pyrrole ring vibration of phthalocyanine. The peaks at 1029 cm^{-1}, 1321 cm^{-1}, 1724 cm^{-1} were attributed due to the sulfonic group. Further a peak at 3465 cm^{-1} was due to –OH stretch vibration of –SO_3H group [44-45]. The FTIR spectra of LDH@MNP revealed a strong peak at 1373 cm^{-1} due to asymmetric stretching vibration of

CO_3^{-2} ions [46]. The peak at 659 cm^{-1} was correlated to the Fe-O stretch of MNPs. The peaks at 3471 cm^{-1} were observed due to –OH stretching of metal hydroxide and inter layer hydrogen bonded water molecules. These interlayer water molecules further exhibited a band at 1637 cm^{-1} due to the bending vibration [47]. After immobilization of CoPcS to LDH@MNP no change in vibration pattern were observed that may be because of low loading.

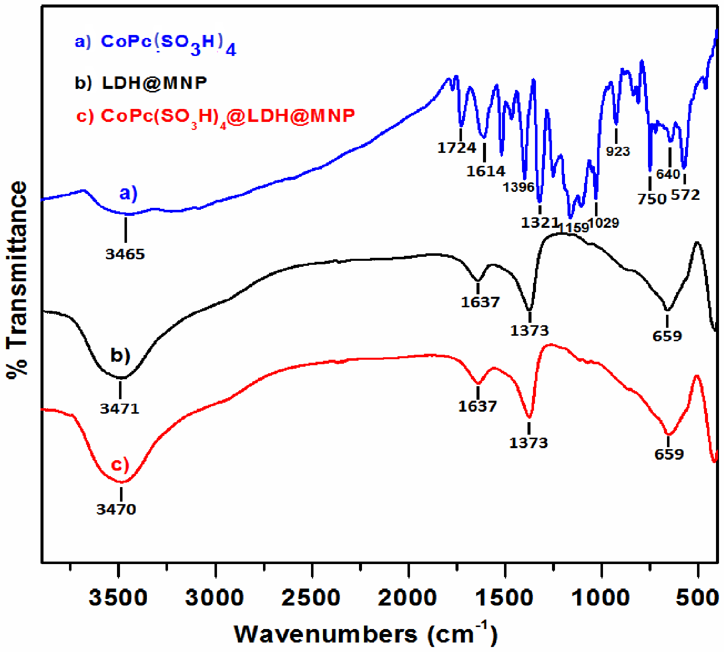


Fig. 5: FTIR of a) CoPcS; b) LDH@MNP; c) CoPcS@LDH@MNP

Thermal stability of LDH@MNP and CoPcS@LDH@MNP was determined by thermogravimetric analysis. The thermogram of MNP's showed a small weight loss at around 100 °C due to loss of moisture and after that no sharp weight loss was observed (Fig. 6a). Thermogram of LDH@MNP showed a small weight loss at 100 °C to 150 °C due to the loss of entrapped water. A very small weight loss around 206 °C was due to loss of exposed –OH groups presented on the outer surface of material. Another major weight loss around 396 °C was assumed due to dehydroxylation and decarbonation [48-50] Fig. 6b. The CoPcS@LDH@MNP catalyst showed similar degradation pattern as LDH@MNP (Fig. 6c). The weight loss due to the attached CoPcS units was not clearly identified which is probably due to the lower loading in comparison to the amount of support.

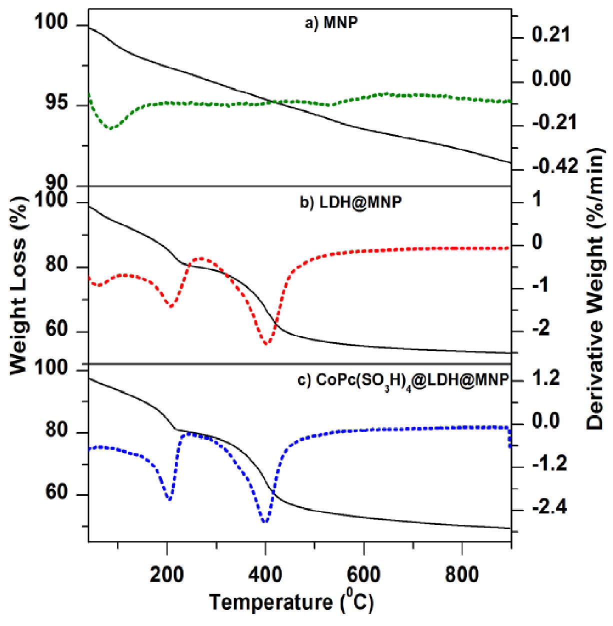
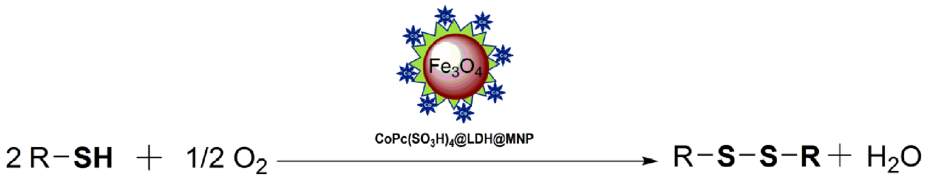


Fig 6: TGA thermogram of a) MNP; b) LDH@MNP; c) CoPcS@LDH@MNP

3.2 Catalytic activity

The catalytic activity of the synthesized heterogeneous cobalt phthalocyanine catalyst was tested for the oxidation of mercaptans in aqueous medium using molecular oxygen as terminal oxidant (Scheme 2).



Scheme 2: CoPcS@LDH@MNP catalyzed aerobic oxidation of mercaptans to disulfides

A wide variety of mercaptans consisting of aliphatic, aromatic, and long chain aliphatic was selectively oxidized to their corresponding disulfides in near quantitative yields without any evidence for the formation of corresponding sulphonic acid. The results of these experiments are summarized in Table 1. The conversion of the mercaptan to disulfide was determined by GC-MS and the identity of the products was established by comparing their spectral data (^{1}H NMR) with those of authentic samples. In general aromatic mercaptans (Table 1, entries 6-9) were found to be less reactive than the aliphatic ones (Table 1, entries 1-5), however in the case of aliphatic mercaptans the reactivity decreases with the increase in chain length and accordingly the mercaptans with longer chain length require more reaction time (Table 1, entries 4-5).

The effect of temperature was also evaluated by considering the oxidation of n-dodecyl mercaptan as the representative reaction (Fig. 7). As shown the oxidation was found to be very slow at room temperature and then the reaction was found to be increased with temperature. Among the various temperatures studied 70 ^{o}C was found to be optimum for this transformation. Further increase in temperature beyond 70 ^{o}C affected the reaction adversely and provided significantly lower yield of the desired disulfide. Further to check the effect of cobalt catalyst, we performed the blank oxidation reaction of do-decane mercaptan using LDH@MNP as catalyst under otherwise identical experimental conditions. The lower obtained yield of the corresponding disulfide (36.4 %) confirmed that the CoPcS units on the LDH@MNP support are the active catalytic sites which provided excellent catalytic activity for this reaction.

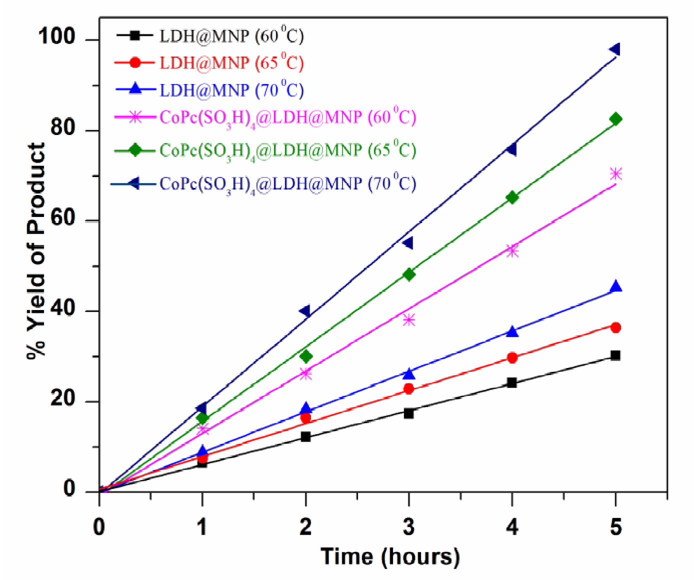


Fig. 7: Oxidation of n-dodecyl mercaptan using LDH@MNP and CoPcS@LDH@MNP at various temerpature

Next, in order to check the practical applicability of the developed catalytic system, we performed the oxidation of kerosene oil sample blended with n-dodecane mercaptan (300 ppm). As shown in Fig. 8, the oxidation of mercaptan in kerosene sample was efficiently occurred and the concentration was found to be decreased from 300 ppm to 89 ppm, 67 ppm and 38.5 ppm at 60 °C, 65 °C and 70 °C respectively.

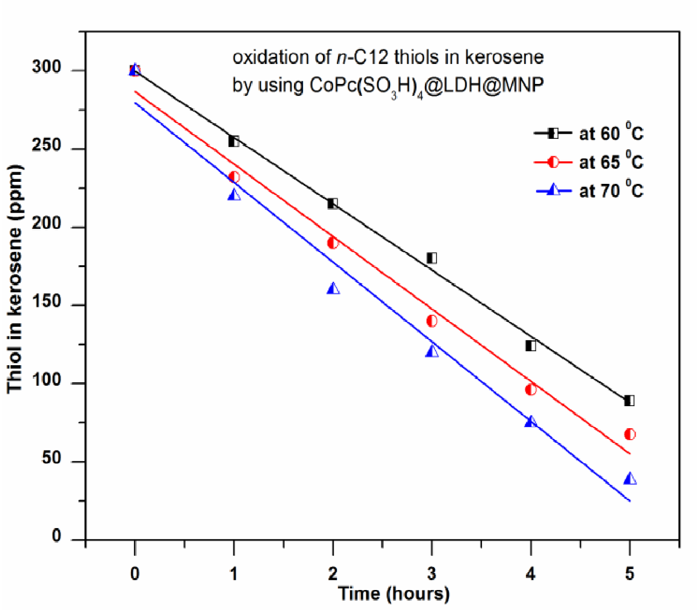


Fig. 8: Oxidation of kerosene blended with n-dodecyl mercaptan using CoPcS@LDH@MNP at various temperature

Magnetic separation of the catalyst as shown in Fig. 9 provides an effective approach for recovering the catalyst from the reaction mixture. At the end of the reaction, the catalyst was recovered by placing a magnetic bar near the glass bottle. The catalyst particles were found to be attracted to the magnet with time increasing and were almost totally attracted after 5 min, leaving a clear solution (Fig. 9). Furthermore, we performed the recycling experiments to evaluate the stability and recyclability of the developed heterogeneous CoPcS@LDH@MNP catalyst for oxidation of kerosene oil sample blended with n-dodecyl mercaptan (300 ppm). The results are summarized in Fig. 10. As shown the recovered catalyst showed almost similar catalytic activity for four runs without showing any significant decrease in the catalytic activity. Moreover, the resulted filtrate samples were analyzed by ICP-AES analysis to determine the leaching of the active CoPcS catalyst during the reaction. The cobalt content in the recovered catalyst was found to be almost same (1.34 wt %) as in the fresh one, indicating that the developed catalyst is quite stable and the reaction is truly heterogeneous in nature.

Fig: 9 Magnetic recoverability of catalyst by external magnet

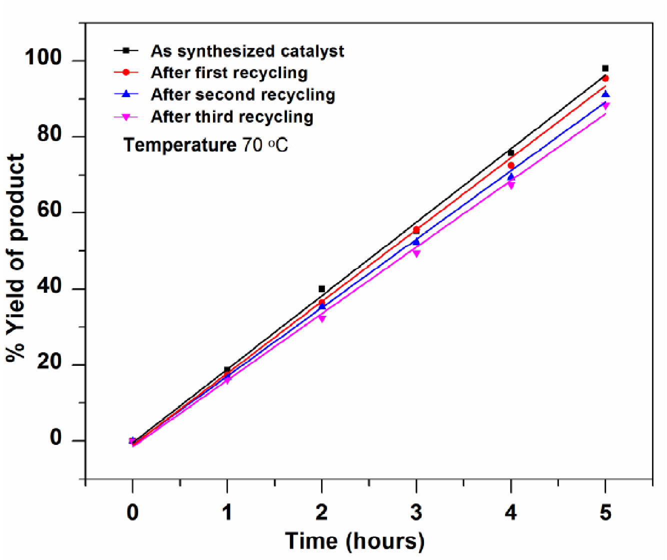


Fig: 10 Recycling experiment at 70 °C for the oxidation of kerosene blended with n-dodecyl mercaptan

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4. Conclusion

We have demonstrated an efficient magnetic nanoparticles coated with layered double hydroxide (LDH@MNP) immobilized cobalt phthalocyanine for the oxidation of mercaptans to disulfides using molecular oxygen as oxidant under alkaline free aqueous medium. The basic sites presented on the LDH surface provided active sites for the covalent attachment of tetrasulfonated cobalt phthalocyanine catalyst. Furthermore, the developed catalyst exhibited excellent catalytic activity for the sweetening of kerosene oil samples which were blended with do-decane mercaptan. After completion of the reaction, the catalyst was easily recovered from reaction mixture by the use of external magnet and reused for several runs with the consistent catalytic activity. Moreover, the presence of magnetic core provided facile recovery of the catalyst from the reaction mixture by using external magnetic effect.

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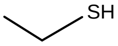
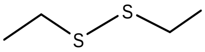
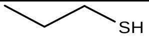
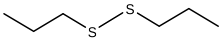
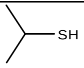
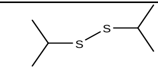
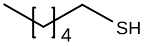
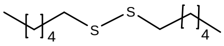
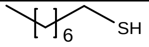
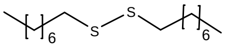
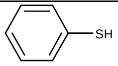
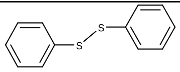
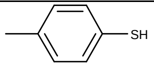
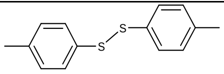
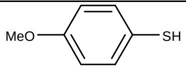
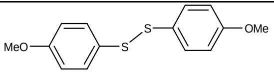
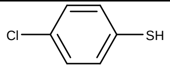
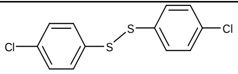
Table 1: Oxidation of mercaptans using CoPcS@LDH@MNP[a]

Entry	Mercaptan	Disulfide	T/h	Conv. (%)[b]	Yield (%)[c]	TOF/ h^{-1}
1.			4.0	97	96	24.0
2.			4.0	96	94	23.5
3.			4.0	94	92	23.0
4.			4.5	94	93	20.7
5.			4.5	90	87	19.3
6.			5.0	88	86	17.2
7.			5.0	87	86	17.2
8.			5.0	84	81	16.2
9.			5.0	81	80	16.0

[a]Reaction conditions: mercaptan (10 mmol), catalyst (0.12 g), water (10 ml) under molecular oxygen at 70 °C; [b]determined by GC-MS; [c]Isolated yield