



## Mercaptan removal from natural gas using carbon nanotube supported cobalt phthalocyanine nanocatalyst



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### ABSTRACT

The synthesis of carbon nanotubes with a cobalt phthalocyanine (CoPc) complex has been described. The removal of mercaptan from gas stream in the present MWCNT-COOH-CoPc nanocatalyst was tested in a fixed bed reactor. For synthesizing this catalyst, multi-walled carbon nanotubes (MWCNTs) were used as support and MWCNT-COOH-CoPc nanocatalyst with loadings of 10 wt% of cobalt phthalocyanine organometal were prepared using the incipient wetness impregnation method. Nanocatalysts were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The effect of important operating parameters including temperature and Gas Hour Space Velocity (GHSV) was investigated. The results confirmed that the best condition can be achieved by setting the temperature at 200 °C and GHSV at 2000 h<sup>-1</sup> with maximum mercaptan conversion of 99.99%.

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## 1. Introduction

Mercaptans and sulfur compounds present in the crude oil and petroleum cuts cause corrosion of pipes and different environmental pollutions. Also in the presence of catalytic processes, they are considered as catalyst poisoning agents. Therefore, it is necessary to remove them by methods that known for mercaptan removal such as: reaction, absorption, adsorption and oxidation (Mikhail et al., 2002).

The main problem these methods, is related to the consumption of significant quantities of solutions and alkali substances, the high cost of catalyst regeneration, corrosive solutions and process selectivity between hydrocarbon removal (particularly for heavy hydrocarbons) and mercaptan removal (Kohl et al., 1997).

Different catalysts for demercaptanization of gas stream have been used in literature such as: active carbon for removal of small amount of methyl mercaptan (CH<sub>3</sub>SH) from air, activated carbon containing dispersed metal oxide particles prepared by carbonization of phenol resin containing metal compounds followed by steam activation, Al<sub>2</sub>O<sub>3</sub> supported Co–Mo (Co–Mo/Al<sub>2</sub>O<sub>3</sub>) and MWCNT supported Co–Mo (Co–Mo/MWCNT)

as hydrodesulphurization catalyst for conversion of mercaptan to H<sub>2</sub>S, the demercaptanization of petroleum or gas condensate by oxidation of mercaptan using oxygen in air in the presence of a base and heterogeneous catalysts containing phthalocyanines catalyst, MgO supported catalyst (MgO/γ-Al<sub>2</sub>O<sub>3</sub>) prepared as solid base by impregnating γ-Al<sub>2</sub>O<sub>3</sub> with magnesium nitrate solution with different MgO loading for oxidizing mercaptan in jet fuel (Tamai et al., 2006; Nakhaei Pour et al., 2010; Mazgarov et al., 1997; Third Revision and Printi, 1975; Tomcala, 2009; Mei et al., 2007).

It is well known that metal compounds especially cobalt (II) phthalocyanine (CoPc) possesses catalytic activity for conversion of mercaptan to disulfides. To the best of our knowledge, no studies on the catalyst with CNTs as support for mercaptans removal from gas stream have been reported. In this study, we report the results of CNT supported CoPc nanocatalyst tests for mercaptan removal from gas stream. Metallophthalocyanine (MPc) carrying an electroactive metal have good electrocatalytic properties (Bedioui and Dodelet, 2006). Porphyrins are ideal building blocks for the design of novel artificial photosynthetic supramolecular systems. In particular, the metalloporphyrins have been of great interest because metal–ligand interactions could provide a convenient way for constructing functional supramolecular arrays. Co(II) tetrasulfophthalocyanine (CoTSPc, Fig. 1) belongs to the N4-macrocylic metal compounds related to the metalloporphyrins with intriguing

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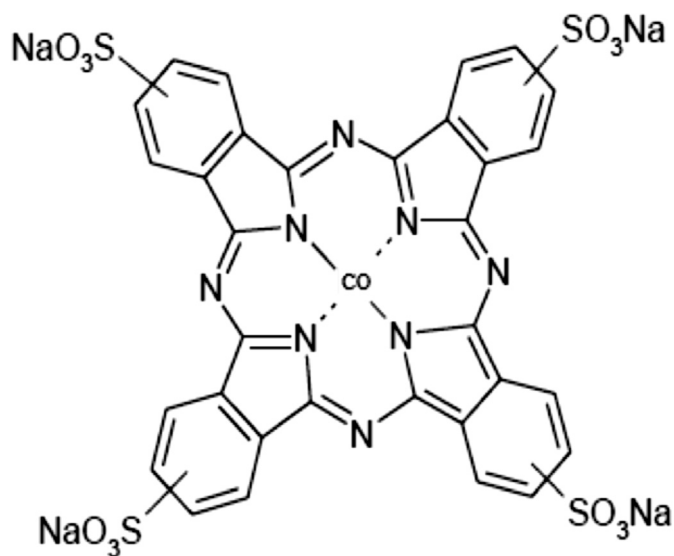


Fig. 1. Structure of the Co (II) tetrasulfophthalocyanine (CoTSPc) organometal.

physical and chemical properties (Leznoff, 1989–1996; Ozoemena et al., 2006; Kadish and Smith, 2003; Bedioui et al., 2007).

Like every other sulfonated metallophthalocyanine (MTSPc) complexes, CoTSPc is a highly water-soluble molecule and very well recognized for its unique physicochemical properties and wide range of applications ranging from catalysis (Ji et al., 2000; Ozoemena and Nyokong, 2002) to sensing and photocatalysis (Flora et al., 2003; Ozoemena et al., 2001; Agboola et al., 2006; Griveau et al., 2003; Snow and Barger, 1989). The major handicap for use of CoTSPc films in heterogeneous electrocatalysis, is its high water solubility (Weber and Busch, 1965; Pirouzman et al., 2008; Oni and Nyokong, 2000; Li et al., 2011). Carbon nanotubes (CNTs) are known to enhance the electrocatalytic properties of metallophthalocyanine complexes (Mugadza and Nyokong, 2010; Mamuru et al., 2010; Wu et al., 2003; Pillay et al., 2010; Wang et al., 2005), thus in this work we integrated nanostructured CoTSPc with multi-walled carbon nanotubes (MWCNTs) with the purpose of enhancing its electrocatalytic properties. Molecules such as phthalocyanines have a great tendency to react with carbon nanotubes. Indeed the curved surface of the carbon nanotube makes their reaction easier with large organic molecules. The interactions between molecules and carbon materials mainly comprise of hydrophobic effects,  $\pi$ - $\pi$  bonds, hydrogen bonds and electrostatic interactions (Yang and Xing, 2010; Britz and Khlobystov, 2006). The reaction between phthalocyanines and carbon nanotubes can be adjusted to lead to a supermolecular structure. Also carbon nanotubes can be functionalized with carboxylic and amino groups in order to increase their ability to chemically link with metal-containing molecular complex and also increase their solubility (Banerjee and Wong, 2002; Chen et al., 1998; Dyke and Tour, 2003).

On the other hand, CNTs are commonly treated with strong acids to improve their poor dispersity into solvents, by which the sidewalls of CNTs were functionalized with carboxylic acid. Therefore, previous studies mainly used the carboxylic acid functionalized CNTs to support metal phthalocyanines as the catalyst (Chen et al., 2010; Schilling and Bron, 2008).

In this study water is used as the solvent. The soluble molecular Co (II) tetrasulfophthalocyanine (CoTSPc) (Fig. 1) was blended with carboxylic acid-functionalized multiwalled carbon nanotubes (MWCNTs) in water to form a stable composite. Consequently COOH-MWCNT scaffold was decorated with phthalocyanine molecules assembled into extended aggregates and orientated

perpendicular to the nanotube surface. This catalyst was then used for mercaptan removal process at different operating conditions.

## 2. Experimental

### 2.1. Materials and reagents

Multi-walled carbon nanotubes (MWNTs) with purity of 90–95% were prepared in Research Institute of Petroleum Industry of Iran (RIPI) by chemical vapor deposition (CVD) method over Co–Mo/MgO catalyst. The average diameter of the nanotubes varies from 10 to 20 nm and their lengths from 5 to 15  $\mu$ m. MWNTs were then functionalized with carboxylic acid group. All solvents including methanol (MeOH), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 96%, nitric acid ( $\text{HNO}_3$ ) 64%, were purchased from Merck Company. Aqueous solutions were prepared using Millipore water from Milli-Q water systems.

### 2.2. Equipment

The demercaptanization tests were performed in a fixed-bed reactor that used for this study and constructed from stainless steel-314 tube 12.5 mm i.d. and 450 mm length. The measurement was done with a KEM potentiometer (AT-500) and UOP 163 method with detection threshold of less than 2 ppm. For sonicating the samples a Fugilab sonicator was used (40–60 kHz). The effectiveness of functionalization procedures were analyzed using Fourier-transform infrared (FTIR) and X-ray diffraction (XRD) spectroscopies. They were used to check the presence carboxylic groups on the MWCNTs surface after acid treatments. The surface morphologies and composite properties of MWCNTs, MWCNT-COOH, MWCNT-CoPC were investigated by field emission scanning electron microscope (FESEM). The morphology of MWCNT and MWCNT-COOH was investigated by TEM.

### 2.3. Synthesis of carbon nanotubes

As mentioned previously, multiwalled carbon nanotubes have been used as the support. They were synthesized using CVD (Chemical Vapor Deposition) process. In this method, carbon nanotubes were prepared over Co–Mo/MgO catalyst in a horizontal reactor from methane decomposition with hydrogen gas as the carrier gas for 30 min at 600–900  $^{\circ}\text{C}$  (Rashidi et al., 2007).

In order to create a better distribution of metal clusters on carbon nanotube, carbon nanotubes should be functionalized. In this study, MWCNTs were functionalized by using acid oxidation method. MWCNTs were added to aqueous acid solution of  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture. Mixture of MWCNTs and acid solution were vibrated in a water bath ultrasonic at temperature of 60  $^{\circ}\text{C}$  for 1 h. After cooling to the room temperature, the functionalized MWCNTs were collected and were washed thoroughly with distilled water. Then this mixture was filtered and washed with deionized water until the neutral pH value of MWCNTs solution was reached approximately to 7. The product was dried in an oven at 90–95  $^{\circ}\text{C}$

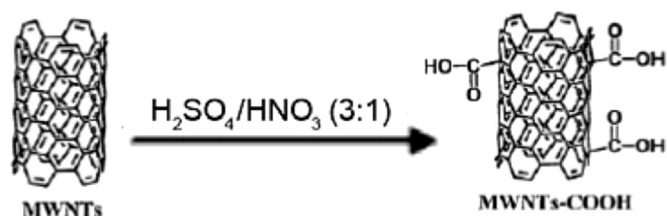


Fig. 2. Chemical modification of carbon nanotubes (CNTs) through thermal oxidation.

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