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SYNTHESIS, CHARACTERISTICS AND KINETIC STUDY AND APPLICATION OF HETEROGENEOUS NANO-CATALYST

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Abstract

Mercaptan removal from a gas stream using multi-walled carbon nanotubes (MWCNTs) supported cobalt nanocatalyst in fix bed reactor is discussed in this paper. MWCNTs as support were first functionalized with carboxylic acid then cobalt particles that are supported by MWCNTs are prepared using impregnation technique.

The nanocatalysts were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. The TEM analysis showed that functionalized MWCNTs were well covered with homogeneously distributed of cobalt particles. The influence of temperature and gas hour space velocity (GHSV) parameters on mercaptan removal under nanocatalysts was investigated. Moreover, the kinetic parameters related to catalytic reaction for mercaptan removal in present of Co-MWCNT nanocatalyst was reported.

The results displayed the concentration of mercaptan from a gas stream is reduced from 16 800 ppm to less than 15 ppm by Co/MWCNTs in temperature of 100˚C and GHSV of 1000 h^{-1}.

Keywords: *nanocatalyst; removal of mercaptan; multi-walled carbon nanotubes; cobalt particles; kinetic study; heterogeneous catalyst.*

1. Introduction

Mercaptans are sulfur-containing organic compounds with the general R-SH formula. They are relatively common in natural gas and petroleum systems as naturally occurring species in low concentrations. Mercaptans are also added to gas products as an odorants for leak examination [1]. Mercaptans a higher concentration become very toxic and may cause harmful health effects. There are difficult methods for removing of mercaptans like as: oxidation, chemical, and absorption. These methods have particular defect and disadvantages, therefore, in order to reduce mercaptans content of stream to desired value must use of the perfect process. Adsorption is one of the most widely applied control technologies for removal of volatile sulfur compounds.

In adsorption procedures for mercaptans removal from gas stream many different catalysts have been applied. Carbon nanotubes as a new type of carbon material have interesting properties such as mesoporosity, high purities, high thermal stability, high surface areas and high pore volume [2-3]. Their morphology and structural characteristics are shown to be quite suitable for use as catalytic support materials and improve catalytic activity and also are insoluble in most organic and aqueous solvents Thus, the surface of CNTs can be modified through different treatment to improve the compatibility and solubility and make a good distribution of metals on their therein [4-5].

In this paper, with an attempt to show the effects of different experimental condition in the removal of mercaptans from gas stream under performance of MWCNT-supported Co nanocatalyst, we functionalized MWCNT- COOH then prepared MWCNT- Co using the impregnation method for produce nanoparticle catalyst, finally used it as catalyst for the adsorption of mercaptans in fix bed reactor.

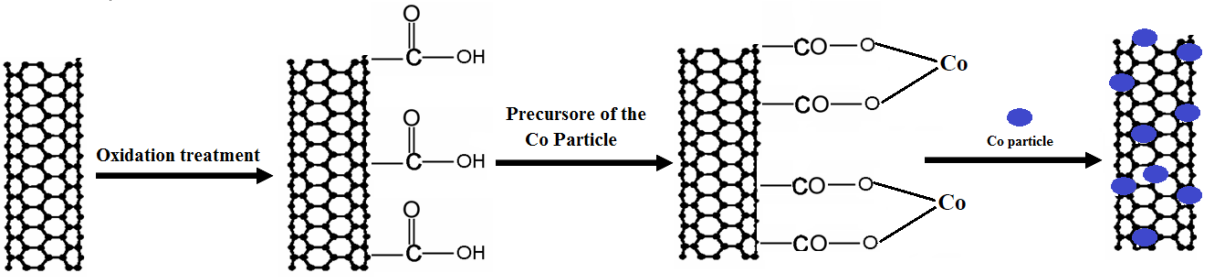
2. Experimental

In section experimental first, MWCNT-supported were prepared by impregnation synthesis method and used as catalysts for mercaptan removal in a fix bed reactor and concentration of mercaptans was measured with a potentiometer. All reagents including sulfuric acid ($H2SO_4$) 96%, nitric acid (HNO_3) 64%, cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$, potassium hydroxide (KOH) were purchased from Merck Company. Aqueous solutions were prepared using Millipore water from Milli-Q water systems. MWNTs Multi-walled carbon nanotubes (MWNTs) with purity > 90%, (size 10 µm; diameter 10 –30 nm; specific surface area 270 m^2/gr and thermal conductivity 1500 w/mv) were prepared in Research Institute of Petroleum Industry of Iran (RIPI) were prepared and MWCNT-Co synthesized using the impregnation method.

In a first step, the carbon nanotubes (CNTs) were synthesized using chemical vapor deposition (CVD) method using (Co-Mo/Mg) catalyst and methane as carrier gas at temperature 900°C for 30 min.

In the next step, carbon nanostructures were functionalized by using acid oxidation method. Carbon nanostructures were added to an aqueous acid solution of H_2SO_4/HNO_3 mixture with the ratio of 1:3 by volume. The mixture is ultrasoniced at a temperature of 60°C for 1 hour then it is filtered and neutralized by being washed with distilled water. The product was dried in an oven at 90ºC for 12 h.

For the synthesis of the metallic nanoparticle of cobalt supported on Multi-Wall Carbon Nanotubes (MWNTs) was used impregnation method. For this purpose, cobalt nitrate was dissolved in a certain volume of distilled water and stirred until a homogenous solution was created, then the resulting solution by the method of impregnation slowly was added to carbon nanotubes. Nanocatalysts was dried at a temperature of 120°C. The chemical structure of MWCNT/Co is shown in Scheme 1.



Scheme 1. Schematic illustration of the synthesis of MWCNT/Co composites

The morphology and structure characterizations of MWCNT, MWCNT-COOH, and MWCNT-Co were performed using transmission electron microscopy (TEM), X-ray diffraction, Fourier transform infrared spectroscopy (FTIR). The tests for mercaptans removal from the gas stream has been accomplished in an operating condition like as reaction temperature and gas hour space velocity (GHSV h^{-1}). The catalyst was loaded in a fixed-bed reactor that constructed from the stainless steel-314 tube. The reactor vertically takes placed in an electrical furnace. The temperature of the furnace was controlled by a thermal indicator controller (TIC).

The gas stream was containing hydrocarbon mixture (98.29wt %) and mercaptan (0.0168 wt %) with mercaptans content of 16 800 ppm. Gas flow to the reactor was regulated by the mass flow controller (MFC). The catalyst was heated from room temperature to the reaction temperature, and amount of GHSV was characterized regarding the volume (mL) of the catalyst and inlet gas velocity (mL/min).

Then the gas stream passes downwards through the catalytic bed. The product stream has been passed through KOH solution (20%) in different times each time for 20 min. The time of the process and operating pressures were 120 min and 1 bar, respectively. Mercaptan concentration is determined by KEM potentiometric (AT-500) titration method according to UOP 163 method. The experimental setup for mercaptan adsorption shows in Fig1.

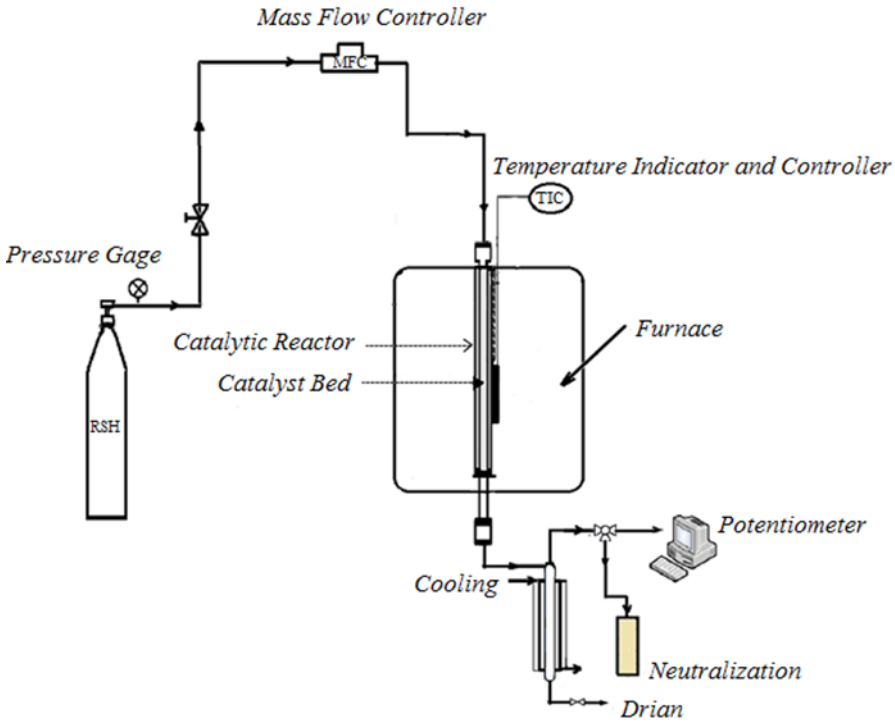


Figure 1. Experimental set-up

3. Results and discussion

The preparation of MWCNT-Co involves the introduction of the MWCNTs of acid groups through sulfuric acid treatment, the development of Co nanoparticles. CNTs are functionalized with functional groups to improve its dispersion into solvents. Acid treatment removes the impurities as amorphous carbon particles and also introduces the –COOH groups on the surface of MWCNTs. The crystallinity formation of Co nanoparticles on the MWCNTs surface is confirmed by X-ray powder diffraction (XRD) results.

The XRD patterns of as-synthesized MWCNTs (a), MWCNT-COOH (b), MWCNT-Co (c) are displayed in Figure 2. The diffraction peaks at 2θ of 26.24° and 42.58° are due to the (002) and (110) planes of MWNTs. As shown in Figure 2(a), 2 (b) XRD patterns of functionalized MWNTs are similar to that of as-synthesized MWCNTs. The intensity of the diffraction peak at (002) in acid functionalized MWCNTs was increased as compared to the as-synthesized MWCNTs. [6-7]

As shown in Figure (2c), two peaks 2θ=26°, 44° is related to the structure of the carbon nanotube, and the rest of the peak is related to the different pages of crystalline Co_3O4. Its dominant peak is in 2θ = 37°, and the other peaks at 45° and 51.5 ° is related to cubic cobalt structures [8-9].

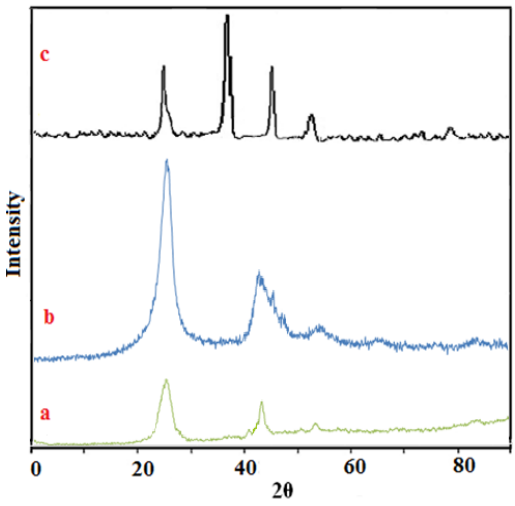


Figure 2. XRD spectra of a) as- synthesized MWCNTs, b) MWCNT-COOH, c) MWCNT-Co

The surface morphologies and composite properties of MWCNTs, MWCNT-COOH, and MWCNT-Co were investigated by transmission electron microscopy (TEM) measurement. The

multiwalled tubes range in length from a few tens of nanometers to several micrometers, and in outer diameter from about 2.5 to 30 nm. The flawless surface in purified condition was clearly observed in TEM image of Fig.3 (a), no destruction occurred on the side wall fig a. Based on the all morphological surface analysis Fig. 3(b), it is mentioned that nanotube functionalization process functionalization leading to shortening and defect to create functional groups on the side wall and at the end of the tube. Fig. 3(c) shows the TEM image of the MWCNTs modified with Co particles. It can also be seen that the f-MWCNTs are well covered with homogeneously distributed of particles because the functional groups on the MWCNT surface cause a uniform distribution of cobalt particles. The average size of Co nanoparticles is within the range of (5-11 nm). Similar to previously reported work, the small particles interact with inside wall and larger particles with an outside wall [10-11].

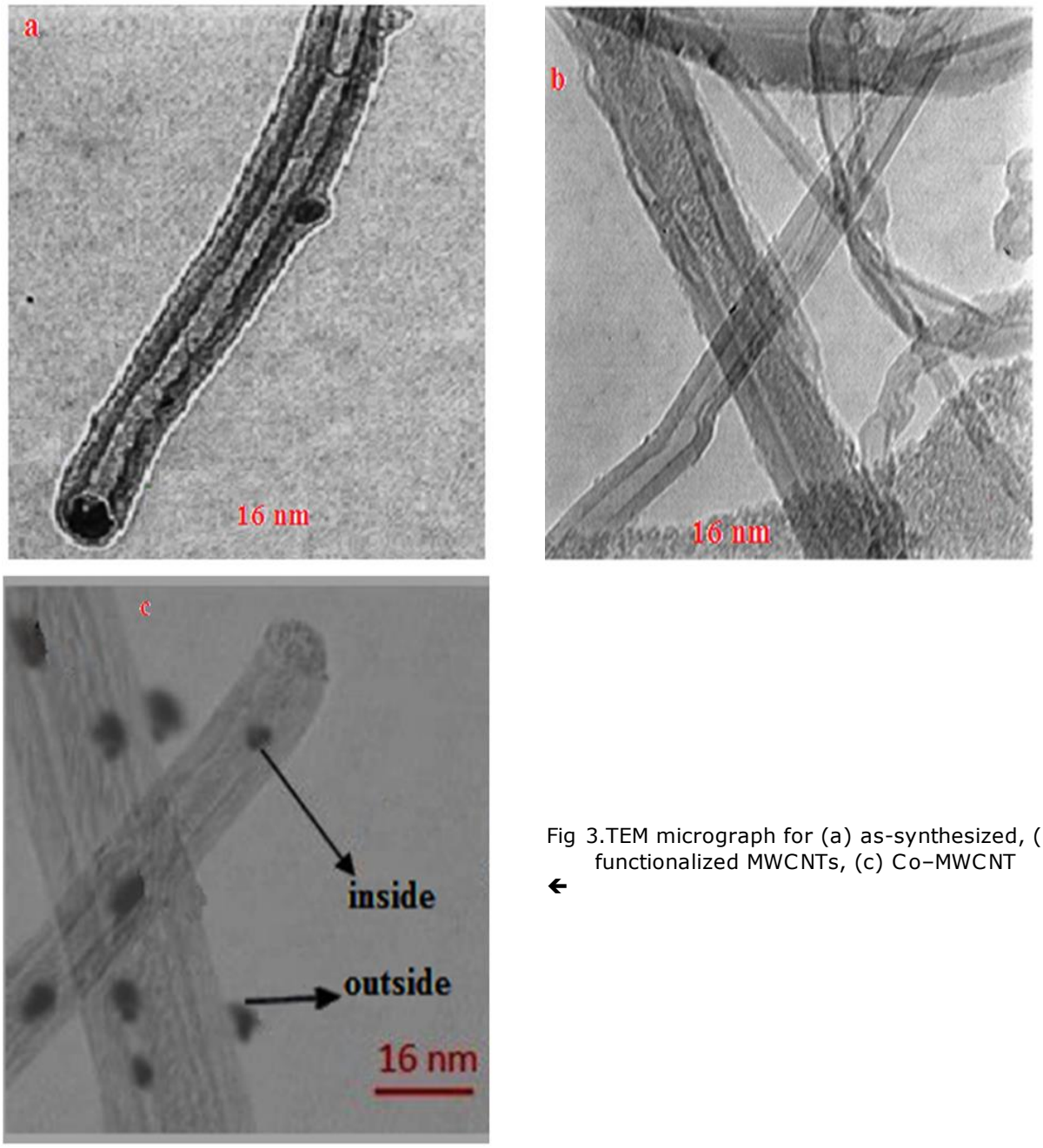


Fig 3.TEM micrograph for (a) as-synthesized, (b) functionalized MWCNTs, (c) Co–MWCNT

Figure 4 illustrates the IR spectra of raw, oxidized and Co- MWCNTs. The IR spectra of raw, oxidized MWCNTs showed similar characteristic peaks, indicating the similarity in the structure of the MWCNTs. These results indicate that after the oxidation step, the oxygen functional groups such as carboxylic and hydroxy acids are formed on the surface of purified MWCNTs.

The FTIR spectra of the pristine MWNTs and after functionalization with carboxylic and MWCNT-Co are shown in Fig (4a-c). Concerning pristine and oxidized MWNTs as shown in Fig (4a, b), the peak at 1570 cm^{-1} is associated with the graphitic structure of CNTs (C=C stretch). The peak at 3400 cm^{-1} is attributed to OH group on the surfaces of pristine MWNTs.The presence of carboxylic C=O (1726 cm^{-1}), C-O (1188 cm^{-1}) and OH

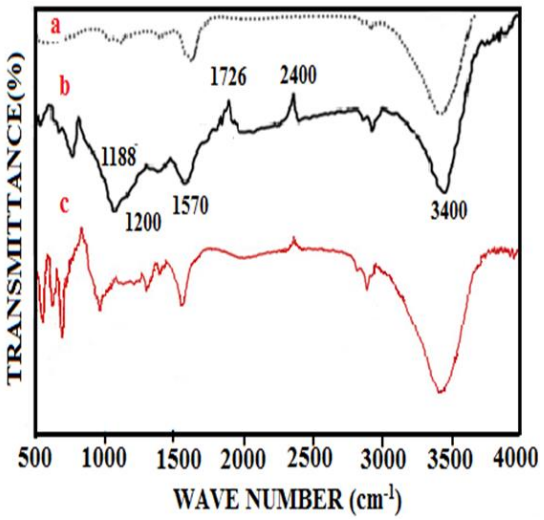


Fig.4. FT-IR spectra of a) MWCNT, b) MWCNT-COOH, c) Co-MWCNT

(2400-3400 cm^{-1}) vibrations in the spectrum of oxidized MWNTs indicated carboxyl groups are formed to the tip and sidewalls of the MWNTs [12-13]. The spectrum of MWCNTs-Co nanocatalyst Fig. 4(C) exhibit the presence of bands at 506, 572 and 660 cm^{-1}. These bands are the feature of a metal–oxygen bond in a spinel-type crystal structure [14].

In compared with MWCNT, there is a slight shift of the skeletal vibration of the graphite sheets for the Co/MWCNT nanocatalyst, which may be due to the introduction of cobalt. Also, the conformational changes observed by shifting of bands in MWCNTs-Co nanocatalyst indicate the formation of stable nanocatalysts by the deposition of Co nanoparticles on the surface of MWCNTs.

The Raman spectra of pristine MWCNTs, MWCNT-COOH, and MWCNT-Co is shown in Figure 5. As can be seen from the Figure 5a, the Raman spectra of the pristine MWCNTs show bands at about 1347, 1573 and 2661 cm^{-1} are the D band, G band and 2D band of MWCNTs, respectively. This strongly supports the fact that MWCNTs were produced. Furthermore, The MWCNT-COOH (Fig. 5b) showed bands at 1352, 1583 and 2750 cm^{-1}. After the junction of cobalt nitrate with MWCNT, the Raman spectrum (Fig. 5c) shows characteristic peaks around 465,671,512 cm^{-1}corresponding to different vibrational modes of Co particles. All the aforementioned characterizations confirm the interaction between Co and MWCNT and matches up well with the reported cobalt oxide spectrum. The relative intensity ratio of the D- and G-bands (I_D/I_G) is used to probe the effectiveness of functionalization. The I_D/I_G band ratios as an indication of the quality of

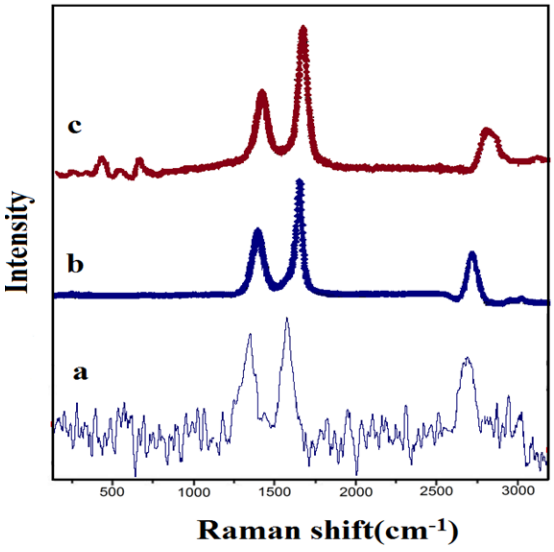


Fig. 5. Raman spectra of a) MWCNT, b) MWCNT-COOH, c) Co-MWCNT

carbon nanotubes for catalyst supports increased with acid treatment. Acid treatment increased the I_D/I_G from 0.11 to 0.19. This shows that the amount of defects on the MWCNT surface increases with acid treatment, which in turn leads to better metal dispersion on the acid-treated MWCNT surface and as well as higher catalyst activity. The formation of particles on the MWCNTs was achieved with some disruption of the graphitic CNTs, and the I_D/I_G varied

to 0.25 for the Co-MWCNT nanocatalyst. It is indicating that some additional disorder was introduced by a synthesis procedure [15-16].

Mercaptan removal from hydrocarbon mixture was carried out under the different operating conditions in the presence of heterogeneous catalyst of Co-MWCNT. The results of some experiments have been shown in Fig.6.

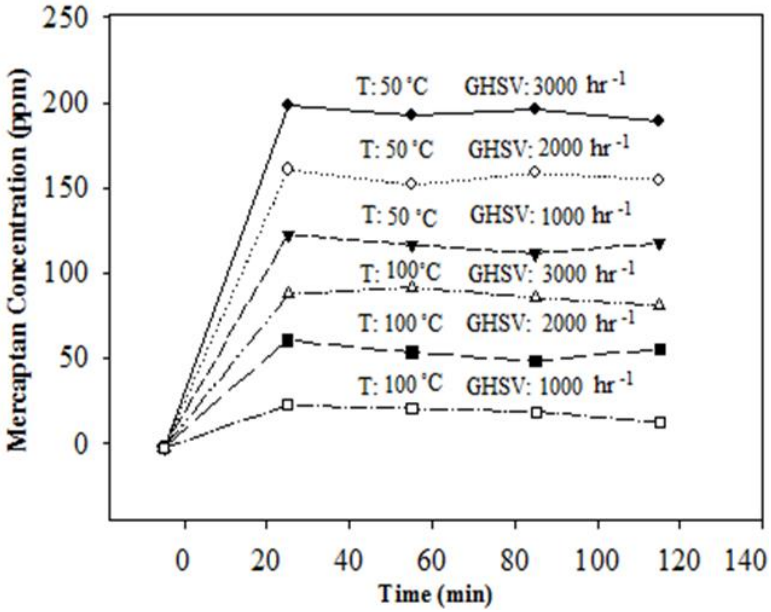


Fig 6. Variation of mercaptan concentration content in exit stream with time

The process was carried out in the temperature of 50 to 100°C and GHSV of 1 000 to 3 000 hr $^{-1}$. In time 0 min mercaptan concentration in outlet stream was 16,800 ppm. At the beginning of the process, maximum adsorption of mercaptan occurs, while after passing time the adsorption process becomes less effective due to saturation of the catalyst surface with mercaptan and as a result mercaptan increases in the exit stream. According to the obtained results, increasing temperature and decreasing GHSV cause better contacting of the gas stream with catalyst and in the result of that better conversion of mercaptan to disulfide. Also, increasing temperature causes an increase in the reaction rate and by increasing the GHSV the residence time of the gas reduces. The maximum concentration of mercaptan in products can be reduced from 16 800ppm to less than 15 ppm under Co - MWCNT nanocatalyst in the best condition of temperature (100°C), and GHSV (1000 hr $^{-1}$).

Mechanism of the oxidation of mercaptan into disulfides in present of Co-MWCNT nanocatalyst are listed below:

The general reaction:

$$RSH \xrightarrow{Ca\ ,O2} RSSR + H_2O \quad (1)$$

Mechanism:

$$RSH + OH^- \leftrightarrow RS^- + HO2 \quad (2)$$

$$RS^- + Co\ (II)\text{-}MWCNT + O_2 \rightarrow RS^-\_\ Co\ (III) - MWCNT\_\ O_2{}^- \quad (3)$$

$$RS^-\ \_Co\ (III) - MWCNT\ \_O_2{}^- \rightarrow RS^0 + Co\ (II) - MWCNT\ \_O_2{}^- \quad (4)$$

$$2RS^0 \rightarrow R\text{-}S\text{-}S\text{-}R \quad (5)$$

In this mechanism, the formation of disulfide result from generation of free radicals (RS^0) which formed from mercaptide ions (RS^-) under Co -MWCNT nanocatalyst. Co (III) -MWCNT are generated by the oxidation of Co (II) -MWCNT by molecular oxygen then the reduction of mercaptide ions by Co (III) –MWCNT gives RS^0 radicals. Finally, the production of disulfides former results in recombination of the RS^0 radicals.

3.1. Estimation of kinetic parameters

Kinetic study of the mercaptans removal lead to optimizing operating conditions, catalyst performance, and determine parameters for better removal of sulfur compounds.

The integral method is a general and better manner for the determination of experimental rates and kinetic parameters of a reaction than the conventional methods. Four models were suggested for the estimation of the order of reaction in term of mercaptan concentration (Table.1).

Table 1. Integrated form of the rate law for rate equation

Order	Rate Law	Integrated Rate Equation
0	Rate= k	$[C_0]-[C_{merc}]=kt$
1	Rate= $k[C_{merc}]$	$Ln([C_0]/[C_{merc}])= -kt$
2	Rate= $k[C_{merc}]^2$	$(1/[C_{merc}]) -(1/[C_0]) = kt$
n	Rate= $k[C_{merc}]^n$	$C_{merc}^{1-n} - C_0^{1-n} = (n-1)\,kt$

n-order, 0, 1 and 2 rate reaction is done using curve fitting then by plotting the power model and experimental data and compare two graphs. It is indicated that the reaction rate is a first-order equation Fig.7.

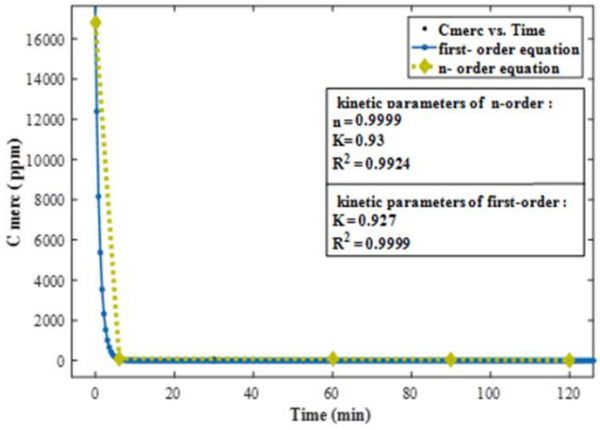


Fig. 7. Comparison n – order equation with experimental data for Co-MWCNT nanocatalyst

Using equations in (Table.1) the data was plotted for each model. The kinetic parameter in the term of R^2 for zero, first and second order guesses are reported in Fig. 8. According to the results, the value of k, n with best-fitted results of R^2 (0.99) for least square is reported for the first-order equation in the present of Co-MWCNT nanocatalyst. Also, it can be concluded that the rate of n, k, R^2 obtained for n – order reaction extremely is similar to the value of n, k, R^2 for first order reaction.

According to Fig. 8, in the first-order reactions the slope is $(-m.K_1)$:

$$\text{Slope} = -m \times K1 = -0.93\ min^{-1} \quad (6) \qquad m = 10^{-3}\ kg / 4 \times 10^{-3}\ m^3 = 0.25 \quad (7)$$

$$K_1 = 0.062\ m^3/Kg\ cat.sec \quad (8)$$

Amount of the activation energy be calculated by Arrhenius' law:

$$K_1 = K_0 \exp(-ER/T) \quad (9)$$

So it's logarithm can be written as:

$$Ln(K_1) = (-ER/T) + Ln(K_0) \quad (10)$$

By having all the other parameters fixed and testing experiments in various temperatures, the amount of the activation energy and the effect of temperature on the rate of reaction is obtained.

Fig.9 indicates the experimental data and the best line that passes through $Ln(K_1)$ versus 1/T for removal of mercaptan under Co – MWCNT nanocatalyst. In accordance with the obtained results, the rate of mercaptan removal reaction intensifies with increasing the temperature.

Thus, the suggested kinetic model of K_1 and the reaction rate equation is presented as follows:

$K_1 = 15.51 \exp(-2049/T)$ (11) and, $-r = 15.51 \exp(-2049/T)[C_{merc}]^{0.99}$ (12)

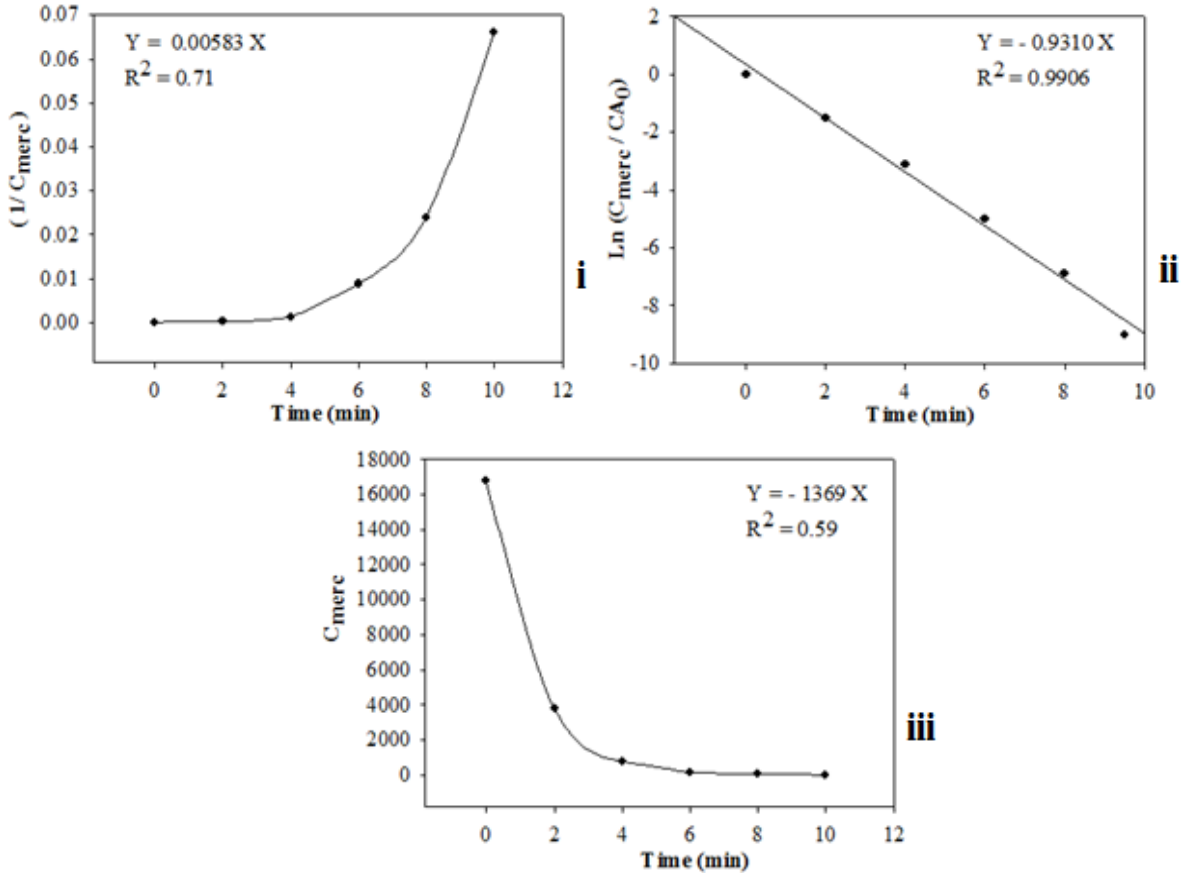


Fig. 8. Estimation of the rate constant of the catalytic reaction using an integral method under Co - MWCNT nanocatalyst for (i) zero-order reaction, (ii) first-order reaction, and (iii) second – order reaction

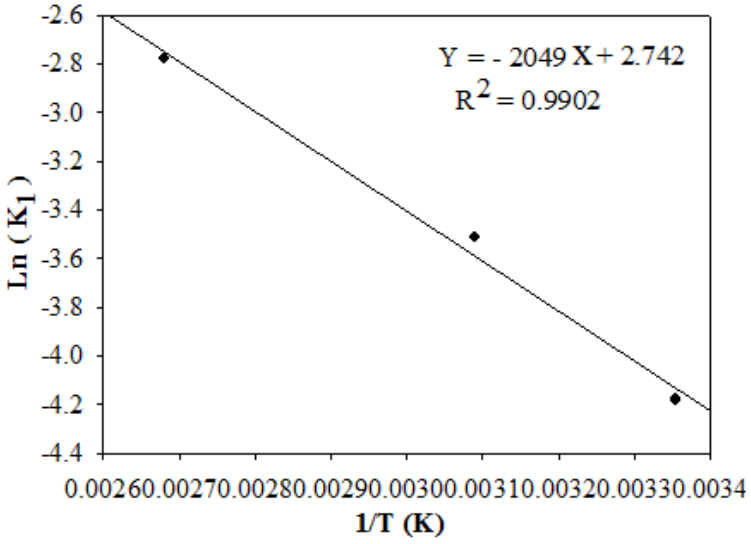


Fig. 9.Arrhenius curve for mercaptan removal in present of Co-MWCNT nanocatalyst

4. Conclusions

Cobalt nanocatalysts that are supported by carbon nanotubes (CNTs) are prepared using an impregnation technique, and their performance in mercaptan removal have been appraised.

The results show that average size of Co nanoparticles is within the range of (5-11 nm) and the small particles interact with inside wall and larger particles with an outside wall. Catalytic test result show mercaptan was removed from a gas stream using Co- MWCNT nano-catalyst. Unreacted mercaptan is reduced with increasing temperature and decreasing GHSV. Decreasing GHSV cause is increasing residence time of gas and better catalytic activity. Temperature has the most effects in mercaptan conversion, and Increasing of it causes an increase in adsorption and reaction rate. In addition, the minimum unreacted mercaptan in outlet gas stream is obtained at a temperature of 100°C and GHSV of 1000 h^{-1} and the concentration of mercaptan under Co-MWCNT nanocatalyst reduced from 16 800ppm of the gas to less than 15 ppm. On the other hand, the kinetic study of mercaptan removal in the present of Co-MWCNT nanocatalyst was investigated, and kinetic parameters related to catalytic reaction for Co-MWCNT nanocatalyst was obtained. By comparing the obtained results for models of 0, 1, 2 and n order of reaction, It was indicated first-order reactions, as the best result, for removal mercaptan in present of Co-MWCNT nanocatalyst in a fix bed reactor.

Nomenclature

E	*Activation energy*	*J. mol^{-1}*
K	*Rate constant*	*mol. m^3.Sec^{-1}.Kg $^{-1}_{cat}$*
k	*Arrhenius' constant*	*mol. m^3. Sec^{-1}.Kg $^{-1}_{cat}$*
r	*Rate of reaction*	*mol. Kg cat. Sec^{-1}. L^{-1}*
R	*Universal gas constant*	*J. mol^{-1} K^{-1}*
T	*Temperature*	*°C*
Time		*Sec*
M	*catalyst weight*	*Kg*
V	*volume of*	*L*
M	*M.V^{-1}*	*kg.m^{-3}*
C	*Concentration of mercaptan*	*mol.L^{-1}*
C_0	*Initial concentration of mercaptan*	*mol.L^{-1}*
Cat	*Catalyst*	
GHSV	*Gas Hour Space Velocity*	*mL.min^{-1}*

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