

# Synthesis of N-CNT-TiO<sub>2</sub> Nanocatalyst: Application in Direct Oxidation of H<sub>2</sub>S to Sulfur

**Daraee, Maryam; Baniadam, Majid\*<sup>+</sup>**

*Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad,  
P.O. Box 91779-48974 Mashhad, I.R. IRAN*

**Rashidi, Ali Morad\*<sup>+</sup>**

*Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI),  
P.O. Box 14857-33111 Tehran, I.R. IRAN*

**Maghrebi, Morteza**

*Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad,  
P.O. Box 91779-48974 Mashhad, I.R. IRAN*

**ABSTRACT:** *In this study, nitrogen-doped MWCNT-TiO<sub>2</sub> nanocatalyst (N-CNT-TiO<sub>2</sub>) with 1, 3, and 5 wt. % nitrogen has been synthesized and its catalytic activity in the oxidation of H<sub>2</sub>S to sulfur has been studied at a temperature of 200°C and O<sub>2</sub>/H<sub>2</sub>S mole ratio of 0.5 and compared with those of neat TiO<sub>2</sub> and TiO<sub>2</sub>-CNT hybrid. Their structure, morphology, and chemical properties have been determined by N<sub>2</sub> adsorption-desorption isotherms, XRD, SEM, TEM, UV, and FT-IR. N-CNT-TiO<sub>2</sub> exhibited improved performance compared with TiO<sub>2</sub>-CNT due to the presence of nitrogen groups. In addition, the nanocatalyst was comparable (up to 5%) with TiO<sub>2</sub> because of the presence of a lower bandgap and synergistic effects. Furthermore, 5%N-CNT-TiO<sub>2</sub> has shown the highest catalytic activity among N-CNT-TiO<sub>2</sub> nanocatalysts due to its higher surface area and pore volume.*

**KEYWORDS:** *N-CNT-TiO<sub>2</sub>; Nanocatalyst; Nitrogen group; Catalytic activity.*

## INTRODUCTION

Hydrogen sulfide (H<sub>2</sub>S) is a poisonous gas which it is produced via many industrial processes such as natural gas, coal gasification and petrochemical plants. From the viewpoint of increasing the standards of efficiency (<7ppm) and environmental protection, the removal of H<sub>2</sub>S from H<sub>2</sub>S containing gases has become very important [1, 2]. The conventional H<sub>2</sub>S removal method, which transforms H<sub>2</sub>S into elemental sulfur, is the Claus process [3]. However,

due to the thermodynamic restrictions of the Claus process, typical sulfur recovery efficiencies are only 90–95% for a two stage reactor [4]. Therefore, direct oxidation of H<sub>2</sub>S to elemental sulfur is used for dilute H<sub>2</sub>S containing gas streams [5,6].

Metal based [7-12] and carbon based [13-15] catalysts are used for removing H<sub>2</sub>S in the direct oxidation process. Metal based catalysts perform better at relatively high

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\* To whom correspondence should be addressed.

+ E-mail: [baniadam@um.ac.ir](mailto:baniadam@um.ac.ir) ; [rashidiam@ripi.ir](mailto:rashidiam@ripi.ir)  
1021-9986/2020/5/131-144 14/\$/6.04

temperatures while carbon based catalysts are required for discontinues processes at lower temperatures [6]. Carbon material catalysts have various applications in catalytic [13, 16] or adsorptive [17] processes. The main disadvantage of carbon based catalysts is their poor selectivity at temperatures higher than 180°C [6, 13, 16]. On the other hand, the insertion of foreign elements into carbon networks has received great remarks during the past decade. Insertion of foreign elements could lead to the significant modification of their intrinsic properties [18-21].

Among the different carbon based catalysts, carbon nanotubes doped with nitrogen are used as catalysts and adsorbents due to the fact that their chemical and physical properties are strongly modified by nitrogen incorporation compared with pure carbon nanotubes. In fact, the acidic-basic properties are modified and the electronic surface state of the support is changed by nitrogen [22]. Nitrogen modifies the carbon and metal interaction with the deposited active phase and thus provides a new catalyst with better efficiency. Indeed, the insertion of nitrogen atoms into the hexagonal network structure of carbon seems to increase the density of the anchorage sites for active phase on the nanotube surface or depositing metal. That leads to the higher dispersion of the active phase nanoparticles and consequently a significant improvement of the overall catalytic activity compared to the undoped CNT [23, 24]. The main advantage of the N-CNT catalysts application against the traditional metal/metal oxide supported ones is that the nitrogen atoms are well anchored within the catalyst structure of the former and thus problems associated with the active phase sintering could be avoided [25].

Nitrogen doped Carbon NanoTubes (N-CNT) have been utilized in H<sub>2</sub>S removal processes by various research groups [16, 26, 27]. N-CNTs is used for the selective oxidation of H<sub>2</sub>S into elemental sulfur and exhibits better catalytic performance compared to Fe<sub>2</sub>O<sub>3</sub>/SiC and Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> at higher reactant gaseous velocity and lower reaction temperature [16]. Also, CNTs and N-CNTs is combined with TiO<sub>2</sub> in photocatalytic applications due wonderful properties TiO<sub>2</sub> [28-31].

In our previous work, TiO<sub>2</sub>-CNT hybrid nanocatalyst was synthesized and its activity in direct oxidation of H<sub>2</sub>S to elemental sulfur was investigated and compared to that of TiO<sub>2</sub> [32]. In this work, TiO<sub>2</sub> was coated on N-CNT and the obtained composite was used as a catalyst for direct

oxidation of H<sub>2</sub>S to S at 200°C and with using mixture of O<sub>2</sub>/H<sub>2</sub>S in ratio equal to 0.5. The influence of nitrogen concentration in N-CNT-TiO<sub>2</sub> catalyst on the desulfurization activity and sulfur selectivity has been investigated and the results have been compared with those of TiO<sub>2</sub>-CNT hybrid and TiO<sub>2</sub> catalysts.

## EXPERIMENTAL SECTION

### Materials

The starting materials for catalyst synthesis, including titanium tetra isopropoxide (TTIP) (99%), isopropanol, and nitric acid (65%), were supplied by Aldrich Chemical Company. Camphor (Merck Chemical Company), Urea (Merck Chemical Company) and Co-Mo/MgO, used as the growth catalyst, were provided by the Research Institute of Petroleum Industry (R.I.P.I.). Distillated water was used in all the experiments.

### N-CNT synthesis procedure

N-doped multi-wall carbon nanotubes were synthesized via catalytic chemical vapor deposition of camphor, urea and Co-Mo/MgO [33] as the carbon source, nitrogen source and growth catalyst, respectively, under hydrogen atmosphere [27]. The reactions were carried out at 1000°C. Urea to camphor ratios were between 1-5 wt. %. The products are nominated to as N-CNT1 (1% nitrogen), N-CNT2 (3% nitrogen) and N-CNT3 (5% nitrogen). The treatment of N-CNTs was carried out in two stages: a) as-synthesized N-CNTs were placed in HCl for 24 h and then b) kept in HNO<sub>3</sub> acid for 6 h. The prepared samples were washed several times with distilled water to reach pH=7. Finally, the samples were dried at 80°C for 12 h in an oven. Synthesis process of N-doped CNT is shown in Fig. 1.

### N-CNT-TiO<sub>2</sub> synthesis procedure

Various ratios of N-CNT-TiO<sub>2</sub> hybrid were synthesized according to the following procedure: N-CNT1 (1wt.%N-CNT), N-CNT2 (3wt.%N-CNT) and N-CNT-3 (5wt.%N-CNT) were added into a mixture of titanium tetra isopropoxide (TTIP) and isopropanol and the mixture was sonicated for 60 min. This solution was nominated as solution I. A certain amount of nitric acid and a specific volume of distilled water were mixed to achieve pH=1 and the obtained solution was nominated as solution II. Solution I was added dropwise to solution II

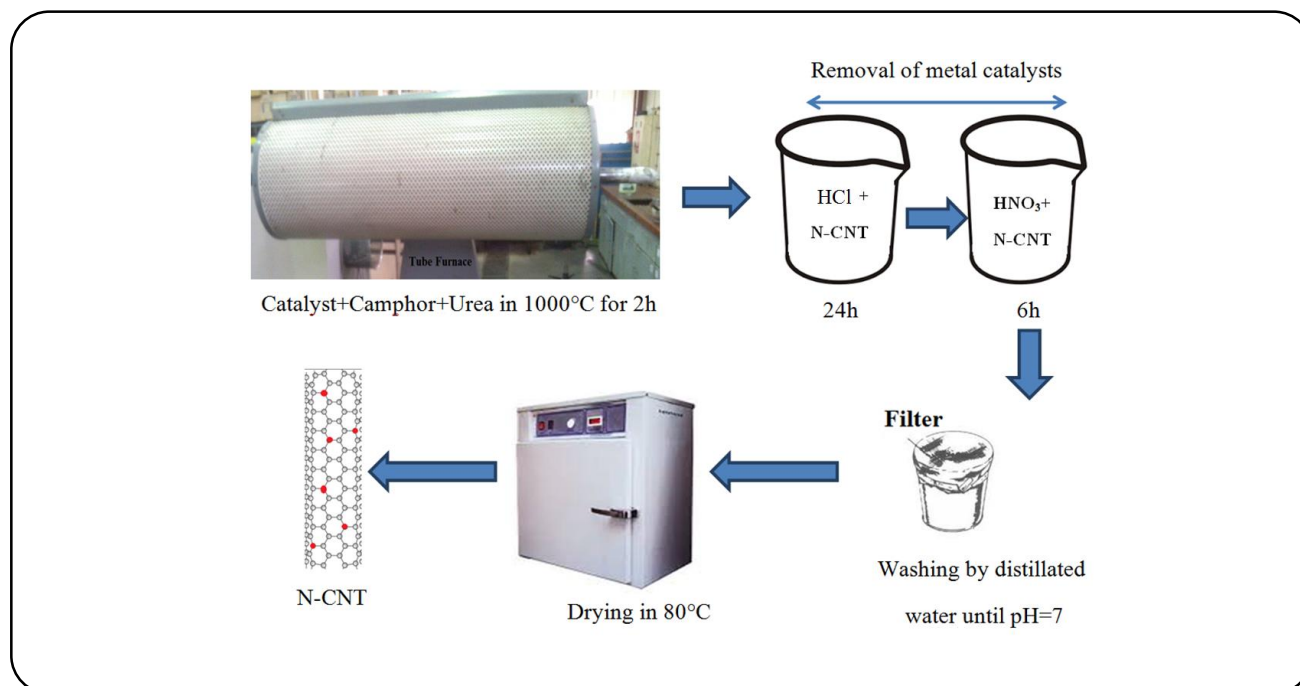


Fig.1: synthesis process of N- doped.

while the latter was being vigorously stirred. The resulting colloidal solution was blended for 2 h to produce a sol, which was then aged for 24 h in an ethylene glycol bath at 80°C and exposed to air for 24 h at ambient temperature to produce a gel. The samples were dried at 110°C for at least 12 h. Finally, the dried samples were calcined in a nitrogen gas atmosphere in a furnace at 400°C for 2 h. N-CNT-TiO<sub>2</sub> synthesis process is shown in Fig. 2.

#### Characterization of N-CNT-TiO<sub>2</sub>

X-ray powder diffraction patterns are registered (XRD, BrukerAXS-D8 Advance X-ray diffractometer high- angle diffraction (10-80)) with Cu K $\alpha$  radiation. Fourier transform infrared (FT-IR) spectra of catalysts were estimated by the KBr method recorded on a Perkin Elmer-Spectrum 65 from 4000 to 600 cm<sup>-1</sup>. Nitrogen adsorption-desorption isotherms were obtained at 196°C using a Belsorp mini automatic adsorption instrument after degassing the samples at 150°C for 5h. Results of isotherms are specific surface area (S) with a Brunauer–Emmett–Teller (BET), V<sub>t</sub> (total pore volume), V<sub>mic</sub> (micropore volume). The morphology and particle size of the catalysts is approved by electron microscopy technique (FE-SEM, VEGA3 TE-SCAN instrument and TEM with Zeiss - EM10C - 80 KV).

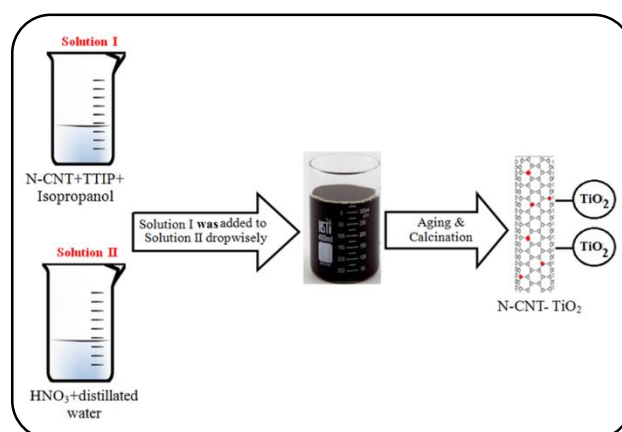


Fig. 2: Synthesis process of N-CNT-TiO<sub>2</sub>.

#### Methods and measurements

Fig. 3 shows the experimental apparatus for the H<sub>2</sub>S removal system. The set up consists of a gas supply unit, a fixed bed reactor in the vertical furnace, and a monitoring system for gas and temperature. The mixture of N<sub>2</sub>, H<sub>2</sub>S and O<sub>2</sub> gases adjusted by mass flow controllers, were passed through the fixed bed reactor. The reactor (1 cm of internal diameter and 50 cm of length) was filled with N-CNT-TiO<sub>2</sub> catalyst. In order to inhibit formation of a hot spot point within the catalyst bed, quartz glass is used. 10 g of the catalyst mixture (2 g of the catalyst and 8 g

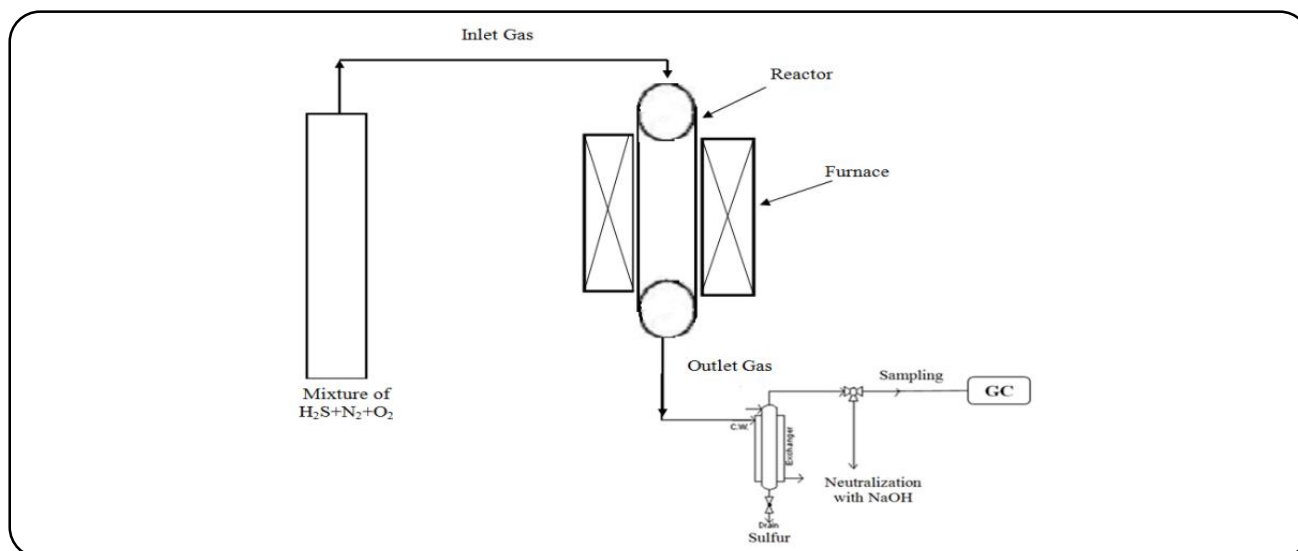


Figure 3: Lab-made apparatus for direct oxidation  $H_2S$  to  $S$  process.

of quartz glass with 30-60 mesh) were placed in the reactor, which was sealed by quartz wool from both sides. The  $H_2S$  and  $SO_2$  concentrations in the reactor outlet were monitored using a gas chromatograph (Agilent 7890b). Equations 1, 2, and 3 show  $H_2S$  conversion, sulfur selectivity and yield, respectively.

$$H_2S \text{ Conversion} = \frac{H_2S_{in} - H_2S_{out}}{H_2S_{in}} \quad (1)$$

$$Sulfur \text{ selectivity} = \frac{H_2S_{in} - H_2S_{out} - SO_{2out}}{H_2S_{in} - H_2S_{out}} \quad (2)$$

$$Sulfur \text{ yield} = H_2S \text{ Conversion} \times Sulfur \text{ Selectivity} \quad (3)$$

## RESULTS AND DISCUSSION

### Chemical composition

FT-IR spectra approve various nitrogen bonds formed in the N-CNT structure. Different nitrogen types formed within the N-CNT structure; that is, N-H, C=N, and N-O, can be attributed to pyrrolic and pyridinic nitrogens and part of pyridinic oxide structure, respectively. All the graphitic, pyridinic and pyrrolic nitrogens have C-N bonds [34].

The absorption bonds of the synthetic N-CNTs are given in Fig. 4 (a, b and c). The FTIR spectrum of characteristic frequencies of pyrrolic N-H, graphitic C-N, pyridinic oxide of N-O and pyridinic nitrogen of C=N are observed for N-CNT1, N-CNT2 and N-CNT3, at 796, 1120, 1384 and 1629  $cm^{-1}$ , respectively. Ghasemy *et al.* has reported the presence of nitrogen peaks [27]. It has been reported that pyridinic nitrogen provides basic sites with the highest catalytic activity for direct oxidation of

$H_2S$  to  $S$  due to its electron pair [13, 16]. In addition, the amount of pyridinic nitrogen formed in the N-CNT structure is one of the important parameters associated with catalytic properties. According to FT-IR analysis, peak intensity of nitrogen groups in 5%N-CNT is higher than other catalysts and it can be related with better performance of 5%N-CNT than 1 and 3% N-CNT in  $H_2S$  oxidation [27].

Fig. 4 (d, e and f) shows the FT-IR spectrum of the synthetic N-CNT-TiO<sub>2</sub>. The adsorbed water molecule peaks due to the stretching vibration of the hydrogen-bonded OH groups is seen in the range of 3000 to 3600  $cm^{-1}$ . The FTIR spectrum of the nanomaterial shows a broad band below 950  $cm^{-1}$ , which is assigned to inorganic Ti-O-Ti network [35]. Graphitic C-N at 1120  $cm^{-1}$ , pyridinic oxide of N-O at 1384  $cm^{-1}$  and pyridinic nitrogen of C=N at 1629  $cm^{-1}$  are also observed. The characteristic peak of Ti-O-Ti is below 900  $cm^{-1}$  which it may overlap with pyrrolic nitrogen of N-H at 780  $cm^{-1}$  and so, N-H peak disappeared. Also, the characteristic peak of adsorbed water molecules is around 1630  $cm^{-1}$  which it may overlap with pyridinic nitrogen of C=N at 1629  $cm^{-1}$ . According to the FTIR results, all N-CNTs have pyridinic oxide or nitrogen, as previously indicated, which could represent their catalytic activity toward  $H_2S$  selective oxidation. The intense peaks reduced with the addition of TiO<sub>2</sub> to N-CNT in Fig. 5 which it shows TiO<sub>2</sub> nanoparticles have been dispersed favorably on N-CNT. Also, peak intensity of nitrogen groups in 5%N-CNT-TiO<sub>2</sub> is higher than other

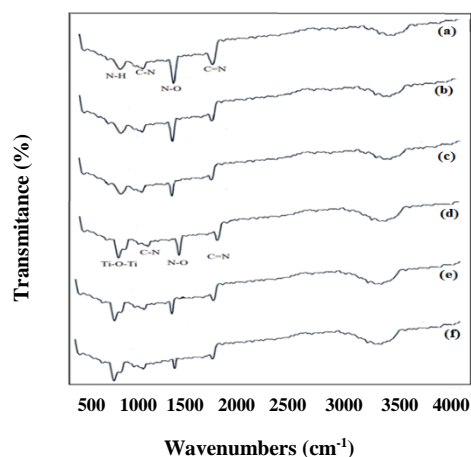


Fig. 4: FT-IR spectra of catalysts: a) N-CNT3, b) N-CNT2, c) N-CNT1, d) 5%N-CNT-TiO<sub>2</sub>, e) 3%N-CNT-TiO<sub>2</sub> and f) 1%N-CNT-TiO<sub>2</sub>.

catalysts and it can attribute to high performance of N-CNT-TiO<sub>2</sub> in H<sub>2</sub>S oxidation.

#### Crystalline structure

The XRD patterns of the neat MWCNT and N-CNT in three different weight percentages of 1, 3 and 5 are shown in Fig. 6 (a, b, c and d). The main peaks at 26.1 and 42.6 are attributed to the (002) and (100) reflections of N-CNT, respectively, which show that the occupied N-CNT is a highly graphitized structure. The XRD patterns of different catalyst are completely similar [22].

The XRD patterns of the N-CNT-TiO<sub>2</sub> are shown in Fig. 7 (e, f and g). The peaks corresponding to N-CNT-TiO<sub>2</sub> hybrid, observed at  $2\theta$  of 25.3, 37.8, 48.0, 55.1, and 62.7°, can be ascribed to (101), (004), (200), (211), and (204) crystal planes, respectively [22]. These peaks are the anatase TiO<sub>2</sub> characteristic diffraction peaks. Notably, no N-CNT diffraction peaks are observed in the N-CNT-TiO<sub>2</sub> hybrid because the main characteristic peak of N-CNT has been overlapped by the main peak of anatase in N-CNT-TiO<sub>2</sub> hybrid [22]. Furthermore, the peaks associated with the growth catalyst are not observed in the XRD patterns [22]. The XRD patterns of different catalyst are completely similar.

The Raman spectrum of N-CNT-TiO<sub>2</sub> and N-CNT is showed in Fig. 7. TiO<sub>2</sub> anatase peaks are appeared at 145, 518 and 640 cm<sup>-1</sup>. Two other predominant bands derived from 5%N-CNTs are appeared at 1378 and 1581 cm<sup>-1</sup> which it could be attributed to the D- and G-bands of N-CNTs, respectively. The Raman spectra showed a clear

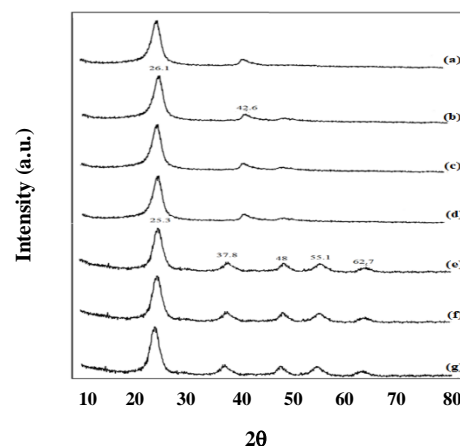


Fig. 6: XRD patterns of catalysts: a) MWCNT, b) N-CNT3, c) N-CNT2, d) N-CNT1, e) 5%N-CNT-TiO<sub>2</sub>, f) 3%N-CNT-TiO<sub>2</sub> and g) 1%N-CNT-TiO<sub>2</sub>.

increase in the intensity of the D-band for 5%N-CNT-TiO<sub>2</sub> compared to 5%N-CNTs, probably due to the influence of interaction between anatase TiO<sub>2</sub> and N-CNTs and the integration of TiO<sub>2</sub> in the N-CNT structure, which diminishes the ordering of the graphitic network [36, 37].

The TGA curves of 5%N-CNT and 5%N-CNT-TiO<sub>2</sub> are shown in Fig. 8. The weight losses of the 5%N-CNT and 5%N-CNT-TiO<sub>2</sub> are around 71% and 58%, which implies to thermal stability of 5%N-CNT-TiO<sub>2</sub> compared to 5%N-CNT. This higher thermal stability of 5%N-CNT-TiO<sub>2</sub> may be related to the presence of TiO<sub>2</sub> [36, 37].

Fig. 9 shows the UV-Vis diffuse reflectance for 5%, 3% and 1% N-CNT-TiO<sub>2</sub> and pure TiO<sub>2</sub>. It can be observed that the 5%N-CNT-TiO<sub>2</sub> catalyst exhibits a stronger visible light absorption compared to other catalysts. In fact, the absorption edge changed towards the longer wavelength. Absorbance edge of TiO<sub>2</sub>, 1% N-CNT-TiO<sub>2</sub>, 3% N-CNT-TiO<sub>2</sub> and 5% N-CNT-TiO<sub>2</sub> nano catalysts are observed at 388, 405, 450 and 463 nm, respectively. Compared with TiO<sub>2</sub>, the presence of nitrogen doped enhances the absorption in the whole visible light region for N-CNT-TiO<sub>2</sub> nanostructures. Furthermore, the absorption of N-CNT-TiO<sub>2</sub> nanocatalyst is higher than that of TiO<sub>2</sub>, which might be attributed to the interaction between N-CNT and TiO<sub>2</sub>. Investigations have been shown that the smaller the band gaps in an oxide have the faster the rate of dissociation and reactivity of hydrogen sulfide and the strength of the H<sub>2</sub>S and oxide interactions depends on the size of the band gap in the oxide metal [38-41]. It is anticipated that the metal or metal

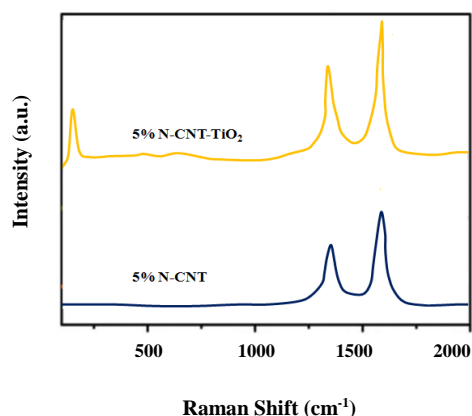


Fig. 7: Raman spectra of 5%N-CNT and 5%N-CNT-TiO<sub>2</sub>.

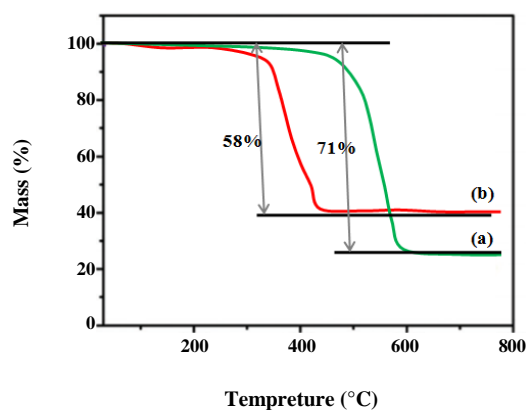


Fig. 8: TGA curves of a) 5%N-CNT and b) 5%N-CNT-TiO<sub>2</sub>.

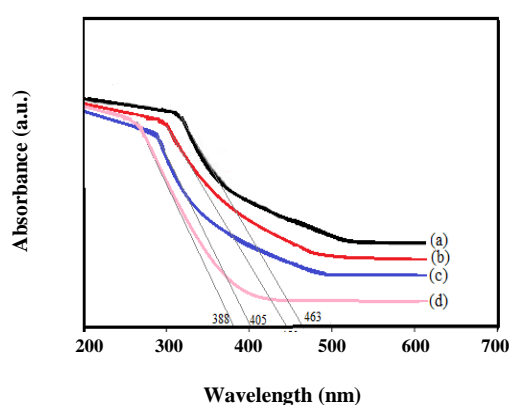


Fig. 9: UV analysis: a) 5%N-CNT-TiO<sub>2</sub>, b)3%N-CNT-TiO<sub>2</sub>, c) 1%N-CNT-TiO<sub>2</sub> and d) TiO<sub>2</sub>.

oxide provides a large number of electronic states that can be very efficient for bonding interactions with S-containing molecules. Orbital mixing can explain the effects of the band-gap size on the reactivity of an oxide and the behavior of metal oxide surfaces in the presence of S-containing molecules. When two orbitals are mixed, final orbital is lower in energy than the initial orbitals and another which is higher in energy. Band gap TiO<sub>2</sub> is high and when N-CNT is added to TiO<sub>2</sub>, the absorption spectra N-CNT-TiO<sub>2</sub> has shifted towards the longer wavelength and the diagram slope has changed and is reduced band gap due to synergetic effect and orbital mixing [42]. On the other hand, TiO<sub>2</sub> is an n-type semiconductor and incorporation with CNTs would lead the flow of electrons to the N-CNTs surfaces. So, the CNTs are acting as electron sinks and TiO<sub>2</sub> is converted to a p-type semiconductor. Here, electrons moved easily from the valence band to the conduction band of anatase TiO<sub>2</sub> due to reduction band gap with addition N-CNT [43]. Therefore, that N-CNTs doped TiO<sub>2</sub> are anticipated to have better performance than TiO<sub>2</sub> for direct oxidation H<sub>2</sub>S to S and 5% N-CNT-TiO<sub>2</sub> is predicted to show the best performance in the direct oxidation of H<sub>2</sub>S to S due to its smaller band gap.

In UV-VIS experimental method, a beam with a wavelength varying between 180 and 1100 nm passes through a solution in a cuvette. The one or more sample component absorbs this UV or visible radiation and then, we scan through various wavelengths in the UV/Vis region of the electromagnetic spectrum. Finally, data is plotted on curve. The x-axis (horizontal) shows the wavelength. The y-axis (vertical) shows the dependent variable the absorbance. We calculated the band gap from UV-Vis spectra of the samples. The band gap energy (E<sub>g</sub>) can be obtained from UV spectrum by the following equation 4 [43]:

$$E_g = 1239.8/\lambda \quad (4)$$

where E<sub>g</sub> is the band gap energy (eV) and λ is absorption maximum wavelength (nm). The calculated maximum wavelength and band gap values are 463, 450, 405 and 388nm and 2.67, 2.71, 3.06 and 3.19 eV for 5% N-CNT-TiO<sub>2</sub>, 3% N-CNT-TiO<sub>2</sub>, 1% N-CNT-TiO<sub>2</sub> and TiO<sub>2</sub>[32], respectively.

#### Surface area and morphology

Figs. 10 (a and b) and 11(a and b) show the BET surface area and BJH plot were done for 5, 3 and 1% N-CNT and N-CNT-TiO<sub>2</sub>, respectively. In this work, total

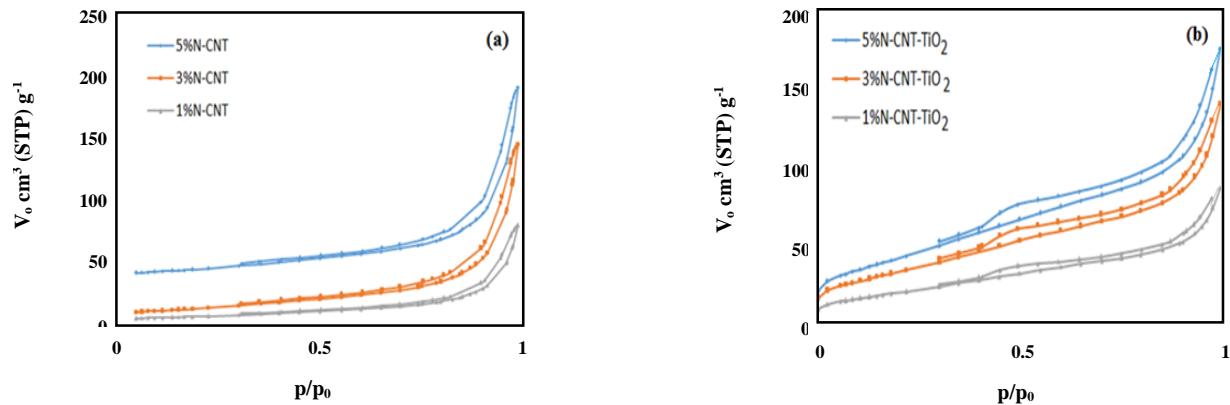


Fig. 10: The N<sub>2</sub> adsorption-desorption isotherms of catalysts: a) N-CNTs and b) N-CNT-TiO<sub>2</sub>s.

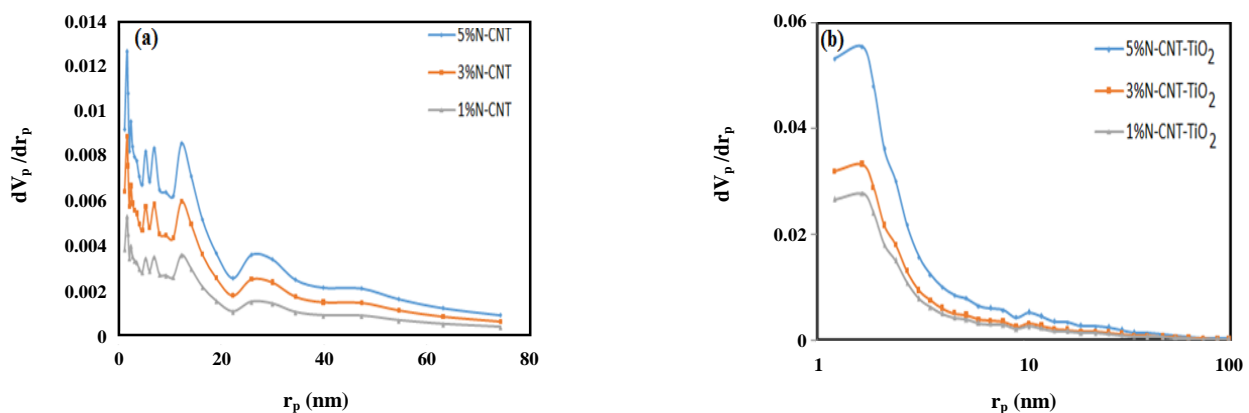


Fig. 11: BJH Plot of catalysts: a) N-CNTs and b) N-CNT-TiO<sub>2</sub>s.

pore volume obtained from the amount adsorbed at  $P/P_0=0.99$  and convert it to liquid volume by  $4V_T/S_{BET}$  with an assumption that the pores are cylindrical.

The surface area was found of 5%, 3% and 1% N-CNT are 54, 43 and 22 m<sup>2</sup>/g, respectively. It can be observed that there are some pores with inner hollow cavities and small diameter in various parts of N-CNT. Furthermore, the catalysts show type IV isotherms (including hysteresis loop) according to IUPAC classification, exhibiting that the synthesized catalysts are mesoporous with narrow pore texture. The BJH analysis indicates that the pore diameter is in the range of 17 to 20 nm for N doped CNTs. The pore size distribution of 5% N-CNT represents a higher degree of porosity than the other two catalysts.

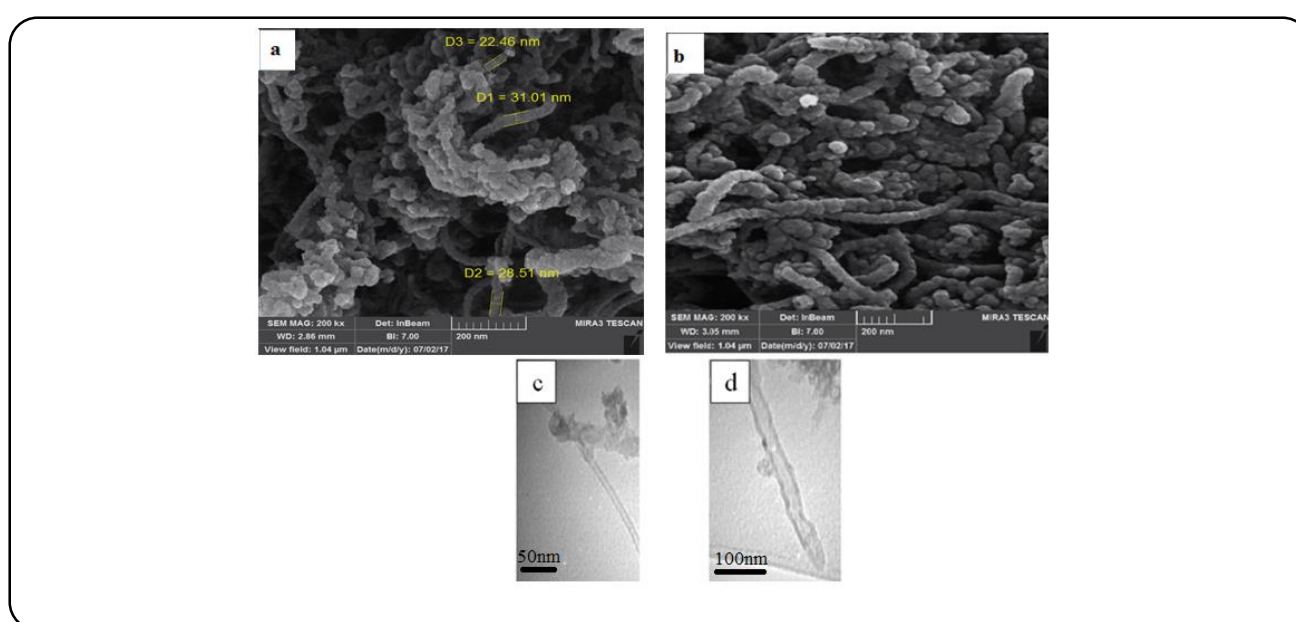
The surface areas were measured of 5%, 3% and 1% N-CNT-TiO<sub>2</sub> are 154, 138 and 112 m<sup>2</sup>/g, respectively. It can be observed that there are some pores with inner hollow cavities and small diameter in all of the N-CNT-TiO<sub>2</sub>

catalysts. In addition, the catalysts show type IV isotherms according to IUPAC classification, exhibiting that the synthesized catalysts are mesoporous with narrow pore texture. The BJH analysis indicates that the pore diameter is in the range of 6 to 8nm for N-doped CNTs. The pore size distribution of 5% N-CNT-TiO<sub>2</sub> represents a higher degree of porosity than the other two catalysts. The interstitial space of N-CNT is anticipated to increase because of irregular nanoparticles of TiO<sub>2</sub> inserted into N-CNT network and the inhibition of agglomeration of N-CNT-TiO<sub>2</sub>. This is in agreement with the FESEM analysis in Fig. 12 and the higher surface area in Fig. 10 for N-CNT-TiO<sub>2</sub> compared with N-CNT. Therefore, the addition of TiO<sub>2</sub> has led the hybrid catalyst to have a higher surface area than N-CNT. Table 1 exhibits the N<sub>2</sub> adsorption-desorption isotherms values for all of the catalysts.

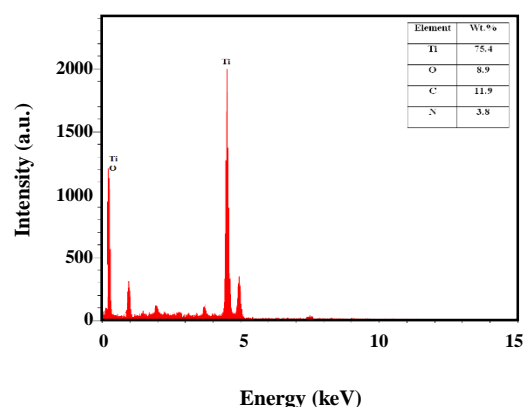
Fig. 12 shows the FESEM and TEM images of bare 5% N-CNT and 5% N-CNT-TiO<sub>2</sub> hybrid, with outer diameters

**Table 1: Surface area, pore volume and pore diameter measurements for all of the synthesized catalysts.**

Catalyst	$a_{s, \text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{gr}$ )	$d$ (nm)
5%N-CNT	54	0.24	18.0
3%N-CNT	43	0.20	20.1
1%N-CNT	22	0.14	17.6
5%N-CNT-TiO <sub>2</sub>	154	0.26	6.9
3%N-CNT-TiO <sub>2</sub>	138	0.23	8.3
1%N-CNT-TiO <sub>2</sub>	112	0.21	6.4
TiO <sub>2</sub> -CNT[32]	304	0.28	3.8
TiO <sub>2</sub> [32]	162	0.14	3.0

**Fig. 12: FESEM micrograph of catalysts: a) 5%N-CNT, b) 5%N-CNT-TiO<sub>2</sub>, c and d) TEM micrograph 5%N-CNT-TiO<sub>2</sub>.**

of 15-25 nm and 20-30 nm, respectively. The nanomaterial has a bamboo-like or tubular morphology with a relatively smooth surface. TiO<sub>2</sub> nanoparticles are almost uniformly coated on the surface of N-CNT in 5% N-CNT-TiO<sub>2</sub> and agglomeration phenomenon does not happen. In fact, the addition of TiO<sub>2</sub> to N-CNT maintains the initial morphology of the catalyst with tubular structure. The TEM image of 5% N-CNT-TiO<sub>2</sub> (Fig. 12 (c and d)) shows that it is fully coated with TiO<sub>2</sub> nanoparticles. The bamboo-like morphology of N-CNT-TiO<sub>2</sub> can also be clearly observed. The surface is entirely and homogeneously covered by TiO<sub>2</sub> nanoparticles. EDX spectrum presented in Fig. 13 further determined the existence of Ti, O, C and N atoms.

**Fig. 13: EDX spectrum of 5%N-CNT-TiO<sub>2</sub>.**



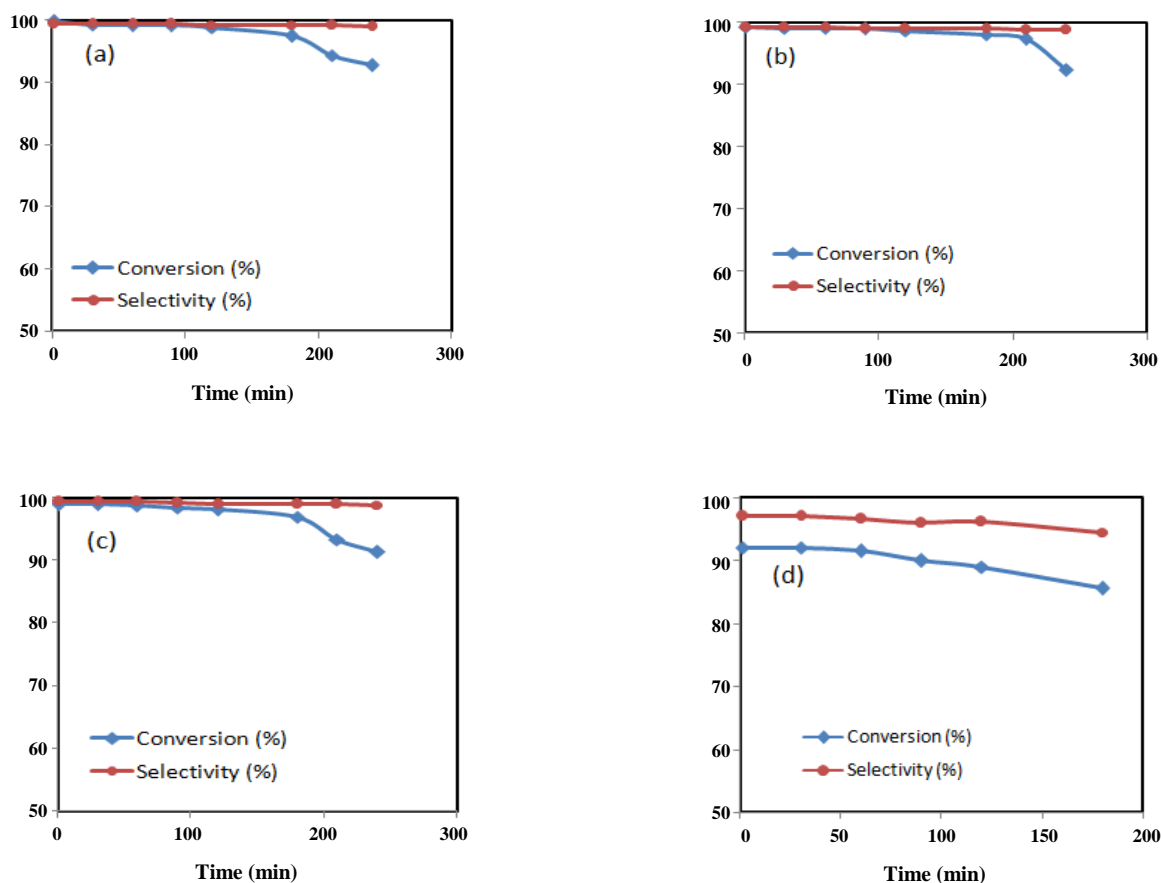


Fig. 14: Catalytic performance of a) 1%N-CNT-TiO<sub>2</sub>, b) 3%N-CNT-TiO<sub>2</sub>, c) 5%N-CNT-TiO<sub>2</sub> and d) 5%N-CNT for direct oxidation reaction in 200°C and O<sub>2</sub>/H<sub>2</sub>S ratio of 0.5.

#### Performance of N-CNT-TiO<sub>2</sub> in direct oxidation H<sub>2</sub>S to S

Fig. 14 shows the performance of three N-CNT-TiO<sub>2</sub> catalysts with 1, 3 and 5 weight percentages of nitrogen in the selective oxidation of H<sub>2</sub>S to S at the optimized temperature of 200°C, O<sub>2</sub>/H<sub>2</sub>S=0.5, for a 4400 ppm feed stream and GHSV of 35000 h<sup>-1</sup>. The results demonstrate that the conversion decreases in the order of 5% N-CNT-TiO<sub>2</sub> (99.7%) > 3% N-CNT-TiO<sub>2</sub> (99.3%) > 1% N-CNT-TiO<sub>2</sub> (99%) > TiO<sub>2</sub>-CNT (98.3%) > TiO<sub>2</sub> (93.5%) > 5% N-CNT (92%). 5% N-CNT-TiO<sub>2</sub> catalyst with 99.7% of H<sub>2</sub>S conversion gives the maximum conversion in 4 h reaction time. The selectivity of all the catalysts was more than 99%. This activity is higher than the value reported by previous investigations [16, 26]. According to our BET results, TiO<sub>2</sub> provides higher surface area for 5% N-CNT-TiO<sub>2</sub> compared to 5% N-CNT catalyst. The particle size of N-CNT in this sample is about 15-25 nm. However, when TiO<sub>2</sub> is coated on N-CNT, the size of N-CNT-TiO<sub>2</sub>

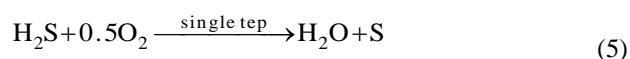
increases to 20-30 nm, so increased surface area with addition TiO<sub>2</sub> to N-CNT. Also, It showed that the adsorption and reaction of H<sub>2</sub>S on TiO<sub>2</sub> anatase (101) surfaces is easier than other phases due to lower energy barrier and the catalytic potential of TiO<sub>2</sub> nanoparticles for H<sub>2</sub>S destruction efficiency is significant at high temperatures[44,45].

According to results, we compared the amount of nitrogenous compounds in different N-CNT catalysts (via FT-IR spectra) and is concluded that 5% N-CNT/TiO<sub>2</sub> present the best performance. Nitrogen species are the most active sites for H<sub>2</sub>S selective oxidation due to their electron density, which provides basic centers for H<sub>2</sub>S dissociation [13, 16]. In addition, the synergistic effects of TiO<sub>2</sub> and N-CNT may cause 5% N-CNT-TiO<sub>2</sub> to perform better than 3 and 1% N-CNT-TiO<sub>2</sub> and TiO<sub>2</sub>. All the N-CNT-TiO<sub>2</sub> catalysts exhibit much higher activity in the direct oxidation reaction compared to the undoped TiO<sub>2</sub>-CNT. 5% N-CNT-TiO<sub>2</sub>

**Table 2: Comparison of H<sub>2</sub>S oxidation for various metal free catalysts.**

Metal free catalyst	Conversion (%)	Selectivity (%)	Temperature (°C)	Reference
Nitrogen-Doped Carbon Composite	95	57	230	46
highly N-doped carbon phase macroscopic supports	99	72	210	47
Mesoporous nitrogen doped CNT	99.5 99.7	86.7 73.4	210 230	27
Mesoporous carbon spheres	100 Poor	100 Poor	Room temperature High temperature	48
N-CNT-TiO <sub>2</sub>	99.7	99.5	200	In this article

has the highest activity due to its higher surface area and pore volume. The results show that H<sub>2</sub>S is selectively oxidized at 200°C and O<sub>2</sub>/H<sub>2</sub>S ratio of 0.5 and there are no side reactions in the presence of 5% N-CNT/TiO<sub>2</sub> catalyst according Eq. (5).



For comparative purposes, recently cited data related to the sulfur capacities of various catalysts are listed in Table 2 for the oxidation of H<sub>2</sub>S containing the major operational conditions for desulfurization processes. In spite of the differences in the experimental conditions, the H<sub>2</sub>S conversion and sulfur selectivity of as-prepared nanocatalysts were higher than the results cited in the literature. Although it should be noted that due to the differences of experimental conditions, this comparison needs to be taken cautiously.

#### **Mechanism of catalytic for H<sub>2</sub>S removal**

The XRD patterns of 5% N-CNT-TiO<sub>2</sub> before and after direct oxidation reaction time of 5 h are shown in Fig. 15. Fig. 16 show Scheme of possible catalytic mechanism of 5%N-CNT-TiO<sub>2</sub> catalyst.

The introduction of nitrogen enhances the hydrophilicity and alkalinity of the CNTs. The hydrophilicity of CNTs in the presence of humidity assists the formation of thin water film. Water is produced in the reaction in the form of steam. The alkalinity boosts the sorption and dissociation of H<sub>2</sub>S into HS<sup>-</sup> ions [50]. Then, elemental sulfur produced by oxidized of HS<sup>-</sup> ions via O\* at the active sites [50]. Sulfur is present in the form of steam at 200°C (above the dew point of sulfur). Since the boiling point in the pores is different from that on

the catalyst surface, it is expected that the deposition of sulfur in the pores of mesoporous catalyst pursues the capillary condensation phenomena [49]. The catalyst is mesoporous and it includes small pore sizes. Thus, sulfur deposition on the catalyst surface causes the pores to plug and decreases the catalytic activity as a function of reaction time. In addition, there is no significant change in the particle size and phase of 5% N-CNT-TiO<sub>2</sub> catalyst after the reaction. This shows that the sintering phenomena may not have happened. The investigation indicated that nitrogen atoms are well anchored within the catalyst structure and thus problems associated with the active phase sintering are not observed [25]. Also, it showed that the adsorption and reaction of H<sub>2</sub>S on TiO<sub>2</sub> anatase (101) surfaces is easier than other phases (rutile and brookite) due to lower energy barrier and the catalytic potential of TiO<sub>2</sub> nanoparticles for H<sub>2</sub>S destruction efficiency is significant at high temperatures. So, it is suggested that the H<sub>2</sub>S dissociation on N-CNT-TiO<sub>2</sub> surface resulting in formation of H<sub>2</sub>O and S [44,45].

In order to investigate the catalytic performance, it is significant to elucidate the catalytic and deactivation mechanism of catalysts. Fig. 15 indicated schematic of deactivation 5%N-CNT and 5%N-CNT-TiO<sub>2</sub> catalyst by deposition of sulfur. XRD of 5 % N-CNT is compared before and after H<sub>2</sub>S oxidation. It is predicted that deposition of sulfur in pores of mesoporous catalyst follow from capillary condensation phenomena. Sulfur is probably deposited in pore volume of N-CNT and N-CNT-TiO<sub>2</sub> catalyst and causes pore plugging. Therefore, the main reason of decreasing catalyst activity is sulfur deposition. However, XRD patterns of TiO<sub>2</sub> before and after use showed that the phase and particle size of N-CNT

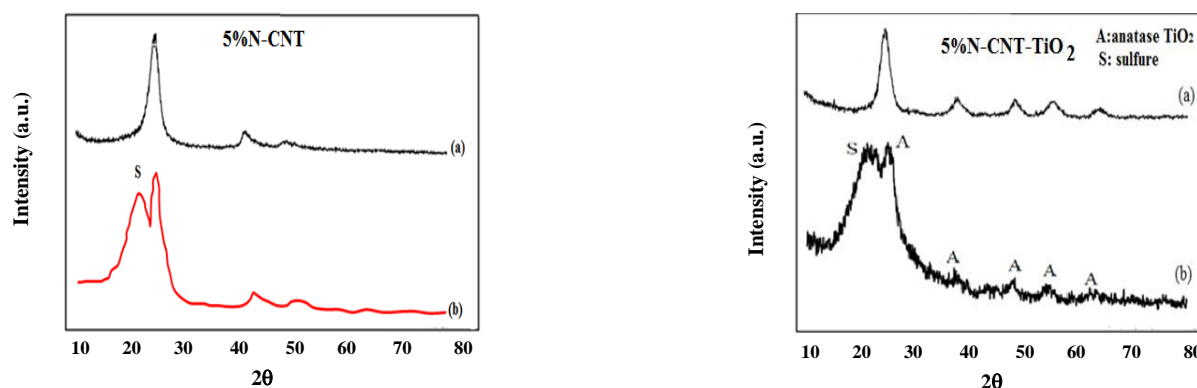


Fig. 15: XRD patterns 5%N-CNT and 5%N-CNT-TiO<sub>2</sub> a) before and b) after direct oxidation reaction time (5 h).

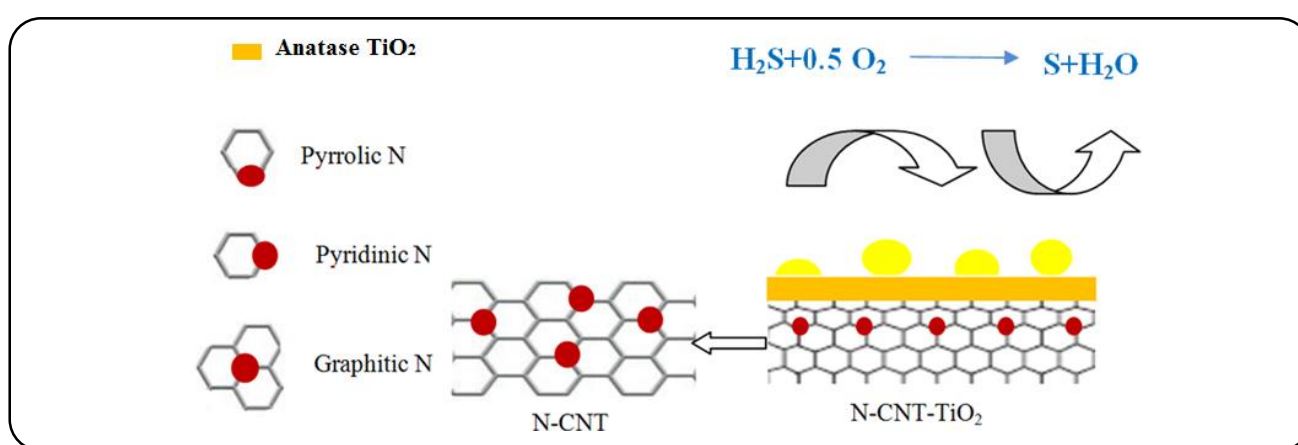


Fig. 16: Scheme of possible catalytic mechanism of 5%N-CNT-TiO<sub>2</sub> catalyst.

and N-CNT-TiO<sub>2</sub> had not changed after the reaction that has suggested that during oxidation considerable sintering don't took place due.

## CONCLUSIONS

In this study, N-CNT-TiO<sub>2</sub> is compared with TiO<sub>2</sub>-CNT hybrid and TiO<sub>2</sub> for removal H<sub>2</sub>S in the reaction temperature of 200°C and O<sub>2</sub>/H<sub>2</sub>S ratio of 0.5. The structure, morphology and chemical properties of the catalysts have been determined by characterization techniques. FTIR and Raman analysis confirmed the presence of nitrogen groups; especially pyridinic and pyridinic oxide species and interaction N-CNT and anatase TiO<sub>2</sub> in the N-CNT-TiO<sub>2</sub> catalyst. The results showed that the insertion of nitrogen atoms into the CNT matrix significantly improved its chemical properties compared to the N free carbon nanotube-TiO<sub>2</sub> and TiO<sub>2</sub>. All of the N-CNT-TiO<sub>2</sub> catalysts exhibit much higher activity in the direct oxidation reaction compared to the undoped ones.

5% N-CNT-TiO<sub>2</sub> has the highest activity (99.7%) due to its higher surface area and pore volume and lower band gap. It was revealed that all of the N-doped CNT with TiO<sub>2</sub> exhibited improved performance compared with TiO<sub>2</sub> due to the lower band gap and synergetic effect.

Received : Apr. 13, 2019 ; Accepted : Jul. 1, 2019

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