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Oxidative desulfurization of petroleum products using oxidized cobalt oxide on the surface-modified carbon nanotubes

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Abstract
Due to the dangerous effects of sulfur in hydrocarbon compounds and its impact on environmental health, a new formulation based on surface-modified carbon nanotubes and a cobalt oxide has been prepared. Oxidative desulfurization was the main reaction of this process that was utilized to reduce this impurity. After the preparation of this nanocatalyst, the TEM images and Thermogravimetric analysis were studied to evaluate the structure of this complex. The results show that the combination of metal oxide and functionalized nanoparticles presents better efficiency in sulfur removal. In addition, the reaction rate raised by increasing the number of functional groups on the surface of nanotubes. The influence of temperature, reaction time and the amount of oxidizing agent in the sample was investigated. The results show that high temperature and high amount of oxidizing agents increase the oxidation efficiency. This phenomena also enhance the efficiency of desulfurization. This finding can be more effective in sulfur removal of hydrocarbons in oil, gas, and petrochemical industries.

Keywords: Surface modification, carbon nanotube, cobalt oxide, desulfurization

Introduction
The use of fossil fuels in different countries is very common that produces a lot of greenhouse gas. Sulfur as a main impurities is presented in these fuels, which causes pollution, acid rain, and large range of respiratory diseases. For this reason, extensive research has been done to remove sulfur compounds from the hydrocarbons[1-4]. Sulfur compounds are found in crude oil as thiophene and its derivatives. These compounds cause many problems in human life and living organisms. In addition, sulfur is the main reason of corrosion in equipments, pipelines, and catalyst poisoning in oil, gas, and petrochemical industries[5, 6] . Therefore, the developed

countries have very strict laws for the allowable amount of sulfur. These values are 10 and 5ppm for gas oil and gasoline, respectively[7] .

There are various ways to remove sulfur from hydrocarbon fuels. One of these conventional methods is the hydrogen desulfurization (HDS). This method has several disadvantages including high economic costs, special equipments, and harsh operating conditions such as high temperature and pressure[2]. Researchers try to economically find a better way with normal conditions. With oxidative desulfurization (ODS) , under normal operating conditions, the highest removal of sulfur (90 to 99.85%) from fossil fuels can be achieved[3, 4].

Due to its unique electrical, physical, mechanical, and chemical properties of carbon nanotubes (CNTs), various attempts have been made to utilize this naoparticle in this processes [8]. Hybrid materials containing metal oxides and CNTs are one of these techniques. Mohammadi et al. used palladium metal oxide and functionalized CNTs under ambient conditions and could remove 90% of sulfur in the fuel [3]. In another study, the molybdenum oxide and surface modified CNTs was investigated to evaluate the desulfurization process. They could take 98% of sulfur removal at 60 ° C in their samples [1].

In this study, the use of CNTs is investigated for the removal of sulfur in petroleum products. We tried to remove sulfur oxides or sulfonates in the presence of an oxidizing agent consisting of a combination of CNT and cobalt oxide. After oxidizing the sulfur in the fuel, the prepared catalyst absorbed the impurities and the sulfur value was measured to demonstrate the quality fuel.

Experimental

The surface modification of carbon nanotubes was performed using acid treatment. Combination of sulfuric acid and nitric acid (3:2, vol/vol) was applied to decorate carboxylic and hydroxyl groups on the surface of CNTs. Next, Co_2O_3 was grafted to this nanoparticle and characterized by TEM images and TGA analysis. After that, the efficiency of the prepared catalysts in sulfur removal was examined. Prepared complex showed better catalyst activity compared to the transition metal oxide. In addition, carboxylic groups play an important role in higher sulfur removal. In different experiments, the effect of temperature, oxidizing amount and contact time were studied. High temperature, large amount of oxidizer and long time increased efficiency. In fact, the high electron density of the synthesized complex facilitates this mechanism.

Results and discussion

TEM Image:

According to our experimental section, surface modification of CNTs (F-CNTS) is one of the key points of this research. It is so important to optimize the surface treatment of nanotubes. Due to the degradation rate and structural changes of CNTs in acid treatment, TEM images were applied to track this procedure. Figure 1b shows clearly the cutting sections of CNTs. These sites are rich in hydroxyl and carboxyle functional groups. In addition, carboxyl groups can oxidize the sulfur impurities and can graft to Cobalt oxide.

Thermogravimetric analysis:

Although TEM shows the active sites of functional groups, but the quantitative value of these functional groups is still unknown. Thermogravimetric analysis (TGA) help up to obtain the exact number of carboxyle groups. Three samples of CNTs with different number of functional groups were utilized in this research. Fig. 3 shows the TGA graphs of these samples. The first one is blonged to pristine nanotubes. Sample 1has the lowest modification (10%) and the third sample has the largest (25%) number of functional groups. Sample two also shows 20 percent drop in mass change when it burns.

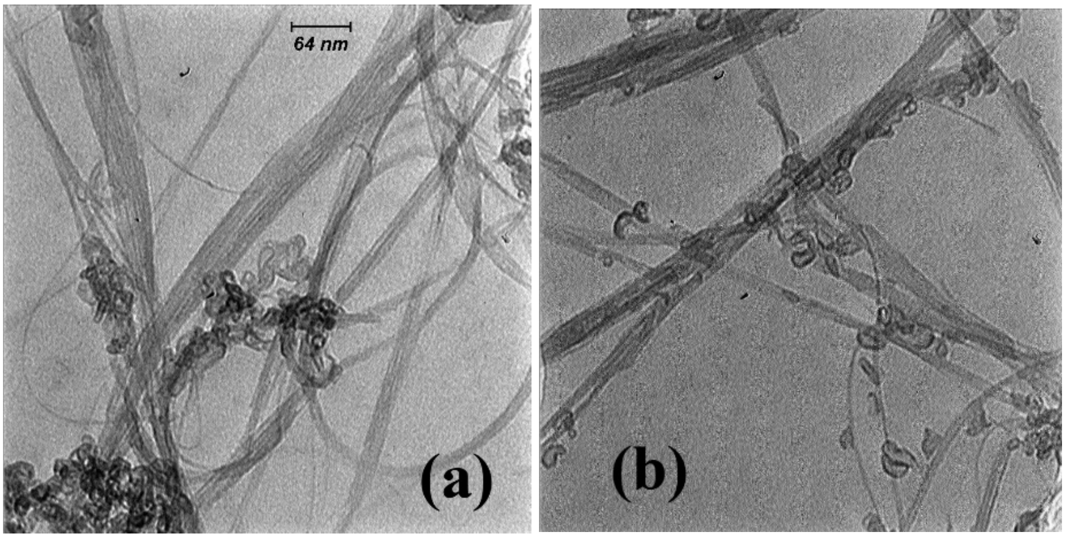

Figure 1: TEM images of (a) pristine CNTs and (b) F-CNTs

Sulfur removal:
In this section, two samples were used to evaluate the capability of sulfur removal in the prepared sample. The Co_2O_3 and F-CNT/Co2O3 catalysts were examined in the same conditions. The synthesized complex could remove 95 percent of sulfur while the cobalt oxide could eliminate 80% of contaminations. This despite the fact that increasing the number of functional groups on the surface of CNTs can improve this value. It is important that surface modification should control during this process. Otherwise, The cylindrical shape of nanotubes will open and physical properties of this nano platform will change.

Effect amount of oxidizing on desulfurization:
To investigate the effect of the amount of oxidant on desulfurization, different amounts of oxidant were examined in different run, the results shown in Figure (2) that as the amount of oxidant increases, the efficiency also increases and the best result was observed in the amount of 0.75 mg of oxidizer.

Effect of temperature and time of oxidant presence:
To determine the best operating conditions for desulfurization, the temperature and time of oxidant presence in the sample were investigated, the results of which are shown in Figure (2). The results show that as the temperature and contact time increase, the oxidizing performance increases and the best performance was observed at 60 ° C and 90 minutes.

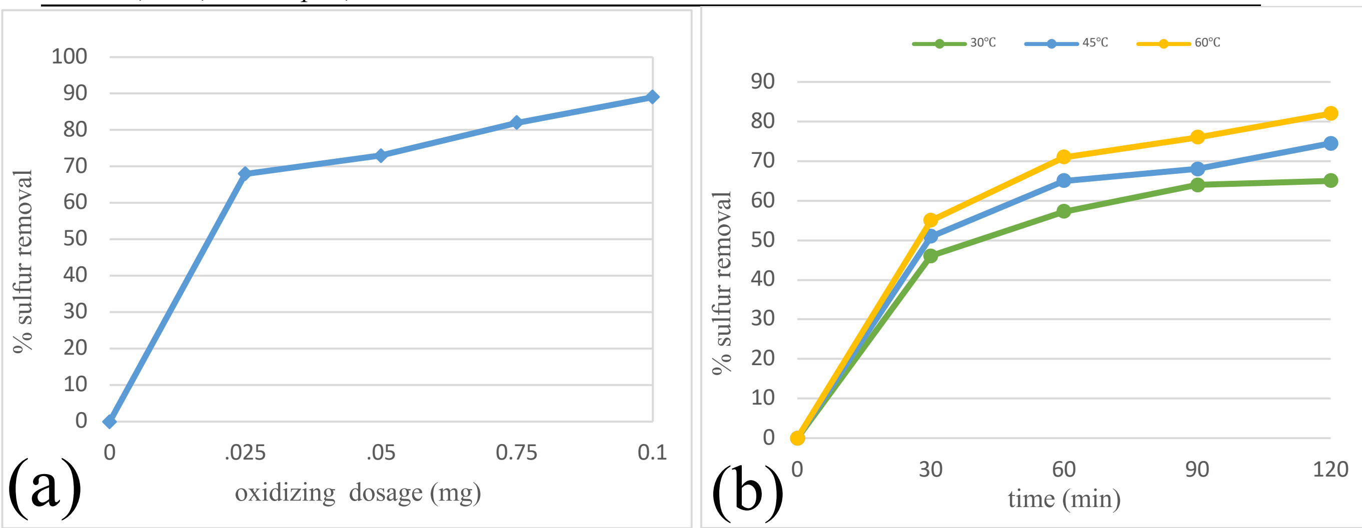

Figure 2: Effect amount of oxidizing on desulfurization(a) - Effect of temperature and time of oxidant presence (b)

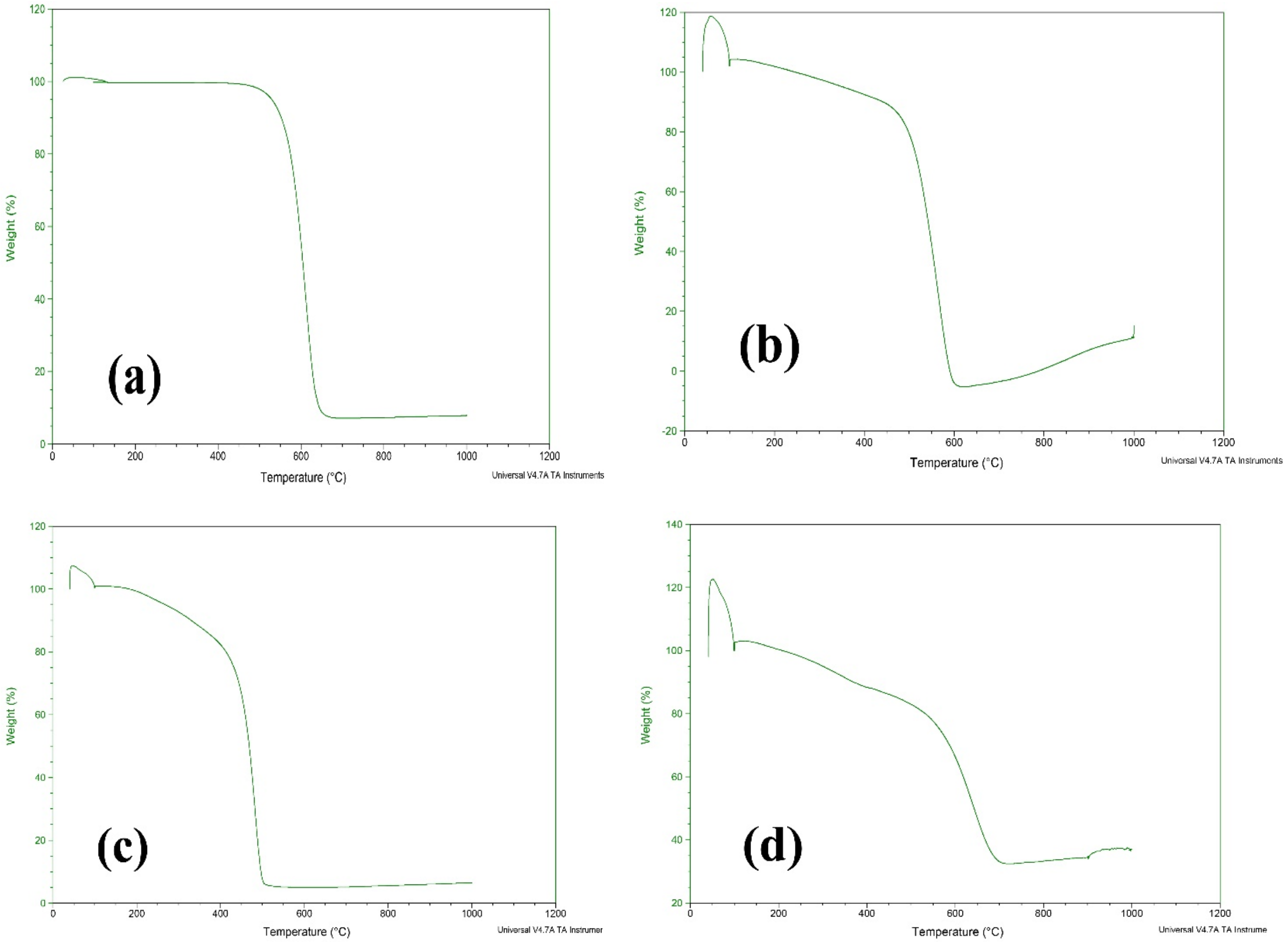

Fig. 3 TGA of : a) pristine CNTs and F-CNTs with different surface modifications b) sample1 , c) sample2 , d) sample3

Conclusions

The ability of new complex based on surface modified CNTs and Cobalt oxide was evaluated in this research. This formulation was used as a new nanocatalyst to remove sulfur compound in gas oil and gasoline. TEM images present a clear change in the structure of CNTs and the TGA analysis calculate the exact amount of this change. In fact, we can estimate the property of nanotubes after this evaluation. This is also important that excess acid treatment can lead to structural opening of CNTs. Next, the Cobalt oxide was grafted to nanotubes and desulfurization of this complex was compared with another sample. The result shows the significant increment in sulfur removal of the complex. This finding can be more effective in sulfur removal of hydrocarbons in oil, gas, and petrochemical industries.

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