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PREPARATION AND COMPUTATIONAL STUDY OF BIMETALLIC COBALT-IRON SUPPORTED ON ALUMINA CATALYST IN CATALYTIC OXIDATIVE DESULFURIZATION

(Penyediaan dan Kajian Pengiraan bagi Mangkin Dwilogam Kobalt-Ferum yang Disokong pada Mangkin Alumina dalam Penyahsulfuran Oksida Bermangkin)

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Abstract

Catalytic oxidative desulfurization (Cat-ODS) is utilized to remove the sulfur content in diesel fuel. Bimetallic catalysts are introduced in the desulfurization process of model diesel fuel, which includes components like n-octane, thiophene (Th), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The presence of dopants was confirmed by atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF). It was found that the addition dopants toward Fe/Al_2O_3 catalyst significantly increased the selectivity of catalytic performance. Using the optimized condition, 98% sulfur removal was achieved. The catalyst's reproducibility test demonstrated that it could be utilized repeatedly for up to five cycles. In addition, mechanism pathways of bimetallic catalysts, both with and without the presence of catalyst have been thoroughly optimized using density functional theory (DFT).

Keywords: desulfurization, catalyst, density functional theory, diesel model, sulfur

Abstrak

Penyahsulfuran oksida bermangkin (Cat-ODS) digunakan untuk menyingkir kandungan sulfur dalam bahan api diesel. Mangkin dwilogam diperkenalkan dalam proses penyahsulfuran bahan api diesel model, yang merangkumi komponen seperti n-oktana, thiofen (Th), dibenzothiofen (DBT), dan 4,6-dimetildibenzothiofen (4,6-DMDBT). Kehadiran dopan telah disahkan oleh spektroskopi penyerapan atom (AAS) dan analisis sinar-X pendaflour (XRF). Didapati bahawa penambahan dopan ke arah mangkin Fe/Al_2O_3 meningkatkan selektiviti prestasi mangkin dengan ketara. Menggunakan keadaan optimum, 98% penyingkiran sulfur telah dicapai. Ujian kebolehulangan mangkin menunjukkan bahawa ia boleh digunakan berulang kali sehingga lima kitaran. Di samping itu, laluan mekanisma mangkin dwilogam, dengan penggunaan mangkin dan tanpa mangkin telah dioptimumkan secara menyeluruh menggunakan teori ketumpatan fungsi (DFT).

Kata kunci: penyahsulfuran, mangkin, teori ketumpatan fungsi, model diesel, sulfur

Introduction

Acid gas combustion produced by the combustion of diesel fuel which released sulfur dioxides compounds to the atmosphere either from industries or transportation can harm the environment and endanger human health [1]. Consequently, the sulfur content in fuels has grown more restricted over the world to overcome these environmental norms and more stringent sulfur control in diesel has been implemented to lower the sulfur content up to 10 parts per million (ppm), known as ultralow-sulfur diesel, wishing to achieve soot-free Euro VI emission standards [2].

Current conventional method in the removal of sulfur, hydrodesulfurization (HDS), is less effective in the removal of aromatic sulfur compounds such as dibenzothiophene (DBT), sulfur compound that mainly exists in fuel oils, and their alkylated derivatives [3, 4]. This technology is restricted since it requires expensive process due to high operational cost, and high operational temperature in the hydrogen gas atmosphere [5]. In order to ensure that the sulfur level of diesel fuels matches the rules, many efforts have been made in searching for a prompt and efficient desulfurization system to overcome the abundance of organosulfur in diesel fuel such as extraction desulfurization (EDS), adsorptive desulfurization (ADS), and oxidative desulfurization (ODS). Among them, catalytic oxidative desulfurization (Cat-ODS) is economically feasible for large scales utilization. When compared to the traditional HDS methods, it needs less capital and has lower running expenses. ODS technology has received a lot of interest since it is useful for creating ultra-low sulfur fuels under moderate circumstances. It can operate under mild conditions due to low temperature and no need for hydrogen gas [6].

Essentially, oxidative desulfurization is divided into two major steps: the first step is the oxidation of compounds consisting of sulfur converted to sulfoxides and sulfones using a selected oxidant. Secondly is the extraction of sulfoxide and sulfone from diesel via extraction, adsorption, and distillation [7, 8]. The efficiency of ODS is greatly dependent on the proper oxidant-catalyst combination. Several oxidants, including tert-butyl hydroperoxide (TBHP), sodium hypochlorite (NaClO), and hydrogen peroxide (H_2O_2), appear to be the best competitors due to their strong oxidizing capacity [3]. Some low-cost metals features, Fe, Zn, and Mo have been discovered to be quite successful in the desulfurization of fuel oils due to their physiochemical properties [9]. According to Bakar et al. [10] pure Fe-Al_2O_3 has a modest oxidative activity and was chosen as a viable option for desulfurization as it requires minimal cost and simple recycling [11].

It has been proven that bimetallic catalysts show higher catalytic activity in the ODS process [12]. Naseri et. al. [13] synthesized bimetallic catalysts composed of molybdenum and zinc. It showed maximal removal of DBT molecules in ODS reaction using the bimetallic catalyst. The same result was observed in the study by Luna et. al. [14] where the bimetallic catalyst using tungsten and vanadium exhibited highest ODS activity. Cobalt is widely known as a catalyst in oxidation processes and hydrodesulfurization [15]. In a previous work, Sampanthar et al. [16] have shown that Mn and Co catalysts were highly active in oxidation of refractory sulfur compounds in diesel using molecular oxygen. The fabricated catalyst can improve the contact surface of the catalyst with sulfur compound. Metal doping would introduce the defects on metal oxides, which in turn plays a significant role in the desulfurization performance. Herein, low valance of Co^{2+} was substituted to the higher valance of Fe^{3+} by the lattice defects [17].

In this study, cobalt was used as a dopant to form bimetallic catalysts. The effect of dopant dosage on catalytic activity was investigated. The mechanistic pathway was postulated and verified by computational study. Co/Fe-Al_2O_3 catalyst was tested for five successive cycles under the optimized condition to ensure the accuracy of the catalytic performance. The fresh Co/Fe- Al_2O_3 catalysts were characterized by atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF).

Materials and Methods

Materials

The catalyst support used was alpha alumina Al_2O_3 beads with diameter of 3-5 mm were obtained from

Sigma-Aldrich. The dopant iron (III) nitrate nonahydrate $Fe(NO_3)_3$ and cobalt (II) nitrate $Co(NO_3)_2$ were used as dopant to synthesize bimetallic catalysts. These dopants were obtained from QRëc. Hydrogen peroxide (H_2O_2) 30% in water (QRëc) and tertbutyl hydroperoxide (TBHP) (70 wt.%) were obtained from QRëc and Across Organics. They were employed as oxidizing agent during ODS process. *N*-octane (99%) was utilized as the solvent for the model diesel fuel, which included thiophene (Th, 99%), dibenzothiophene (DBT, 97%), and 4,6-dimethyldibenzothiophene (4,6-DMDBT, 95%). *N,N*- dimethylformamide (DMF) from MERCK was used as extraction solvent to remove sulfur impurities.

Catalysts preparation

Bimetallic catalysts based with different Fe and Co metal loadings were prepared by incipient impregnation method on Al_2O_3 beads. 4g of alumina support was immersed into the 2g of $Fe(NO_3)_3$ solution until complete absorption occurred on the surface. The mixture was put onto the glass wool and dried in an oven at 100 °C for 24 hours. The furnace was set up at the temperature of 400 °C and the catalysts was heated for 5 hours to ensure all the metal counter ions and water molecule are removed. The cobalt-iron supported on alumina catalyst was prepared by doping with $Co(NO_3)_2$ after the successful impregnation with iron using the same impregnation method. A series of bimetallic catalysts with different Co salt loading was synthesized (10, 20, and 30 wt.%). The developed catalysts were designated as follows Co/Fe-Al_2O_3 (10:90), Co/Fe-Al_2O_3 (20:80), and Co/Fe-Al_2O_3 (30:70). Based on AAS analysis, it shows that there are slightly differences in active species concentration compared to theoretical calculation this might because AAS analysis fully characterized the elemental composition of the material [18]

Oxidative desulfurization and characterisation

The 500-ppm model diesel fuel was formulated with three model sulfur compounds: thiophene (Th), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in *n*-octane solvent. Model diesel fuel (10 mL) was added to the round bottom flask, together with catalyst (0.1g) and TBHP oxidant (O/S= 3).

The ratio of S molar ratio and TBHP is (1:3) (m/v). The mixture was refluxed for 30 min with intense stirring. The resulting mixture was cooled and filtered. The oxidized diesel fuel was extracted by solvent extraction (DMF) in a 1:1 diesel-to-solvent ratio (v/v). The extraction process was rapidly agitated at room temperature for 30 minutes before the diesel and solvent phases separated. Gas chromatography (Agilent 7890A) with a flame ionisation detector (GC-FID) together with equity 5 column were used to measure the sulfur content. The synthesized catalysts were further characterised using atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF) to analyse the elements presence in the catalyst. The textural properties of the catalyst and support were analyzed by nitrogen physisorption isotherms. N_2 adsorption-desorption isotherm was performed on Micromeritics ASAP 20120 adsorption analyzer at -196 °C. The equilibrium geometries and energy of the intermediates in the hypothesised process were calculated using density functional theory (DFT). All the energy calculations in this paper were done with the Gaussian 09/Gaussian 16 programme.

Result and Discussion

Atomic absorption analysis (AAS) was performed using the direct approach to assess the total metal content in Co/Fe-Al_2O_3 catalyst. The analysis of AAS in (Table 1) confirmed the presence of Fe and Co elements for all the catalysts. The Fe and Co metal content of the bimetallic catalyst were found to be in the targeted range. The trend for Co loading is an agreement with XRF analysis.

The large quantities of weight percentages of all elements were determined using XRF analysis in comparison to the nominal weight percentage introduced to the system, and the results were illustrated in Table 2. From XRF data measurement, the actual weight percentages for the elements in Co/Fe(10:90)/Al_2O_3, which was calculated for the preparation of Co and Fe were 15.8 wt.% and 84.2 wt.%, respectively. The percentages detected were found to be lower for iron species in Co/Fe(10:90)/Al_2O_3 due to the presence of other elements in the sample matrix and affecting the accuracy of the analysis. These matrix effects can lead to a lower measured percentage for the target [19]. Even though there was a variation in AAS and XRF measurements, the data remained compatible with results acquired with more precision [20] From the XRF data, the amount of every element calculated was approximately similar to theoretical calculation. Thus, it evidenced that all the elements were present and dispersed well on the catalyst support. From our previous publication, XRD analysis proved the presence of oxide phase of Fe_3O_4 and Co_3O_4 in the catalyst [21].

Table 1. The concentration of metal element in Co/Fe-Al_2O_3 catalyst

Catalyst	Calcination Temperature (°C)	Concentration (ppm)	
		Fe	Co
Co/Fe-Al_2O_3 (10:90)	400	0.055	0.025
Co/Fe-Al_2O_3 (20:80)	400	0.030	0.057
Co/Fe-Al_2O_3 (30:70)	400	0.026	0.061

Table 2. Composition of metal element in Co/Fe- Al_2O_3 catalyst

Catalyst	Element (wt.%)	
	Fe	Co
Co/Fe-Al_2O_3 (10:90)	84.2	15.8
Co/Fe-Al_2O_3 (20:80)	80.6	19.4
Co/Fe-Al_2O_3 (30:70)	70.0	30.0

Effect of dopant ratio

The study was carried out to investigate the removal of sulfur compounds from model diesel fuel over Co/Fe-Al_2O_3 catalyst by using different dopant ratios of Co and Fe, calcined at 400 °C in a range of 10:90, 20:80, 30:70, and the results are presented in (Figure 1). The Co/Fe ratio of 10:90 gave the highest conversion of DBT (100%), 4,6-DMDBT (79%), and thiophene (93%). The variability in reactivity of sulfur compounds is mostly due to differences in electron densities on the sulfur atom and the sulfur compound's steric hindrance. Th, DBT, and 4,6-DMDBT contain electron density on the sulfur atom of 5.696, 5.758, and 5.760, respectively [22]. The removal of 4,6-DMDBT is the lowest compared to Th and DBT, since there is a methyl group presence on 4,6-DMDBT that acts as an obstruction for sulfur atom to take an approach to the catalyst's active core. An excess of cobalt concentration may form a cluster of active species on the catalyst's surface and reduced its surface area. The high amount of cobalt also prevented the Fe active sites from being equitably distributed across the supported catalyst surface, causing the catalyst's activity to become distorted [23]. Previous research had shown that Co loading can result in variable active surface site [24], and the catalytic characteristics were shown to be reliant on the dispersion and engagement of the Co with the support [25].

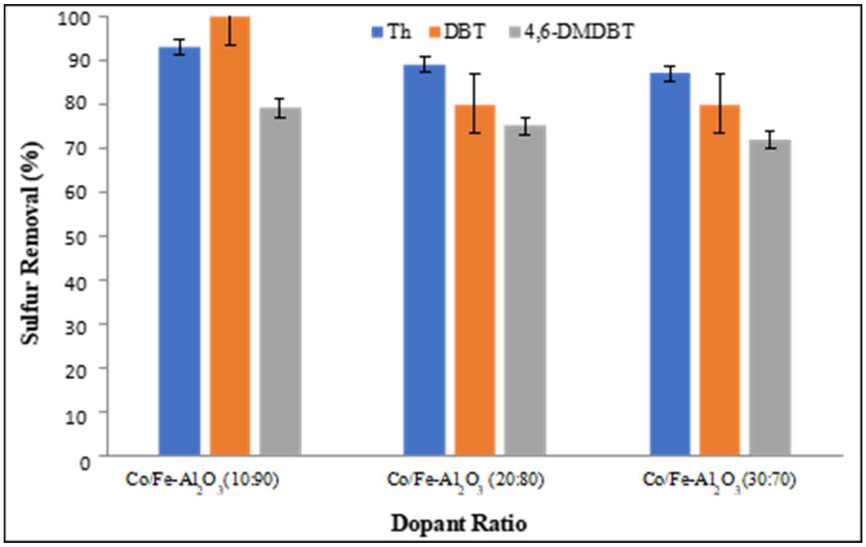

Figure 1. The impact of catalyst doses (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF)

Repeatability test

The repeatability investigation was performed three times to ensure accuracy. The catalytic activity of these catalysts was studied under similar preparation and experimental conditions. The outcome of three repetitions of Co/Fe(10:90)-Al_2O_3 catalyst repeatability testing as illustrated in (Figure 2). The observation showed there were not much difference in the repeatability test for the model diesel sample, indicating the accuracy of the analysis performed.

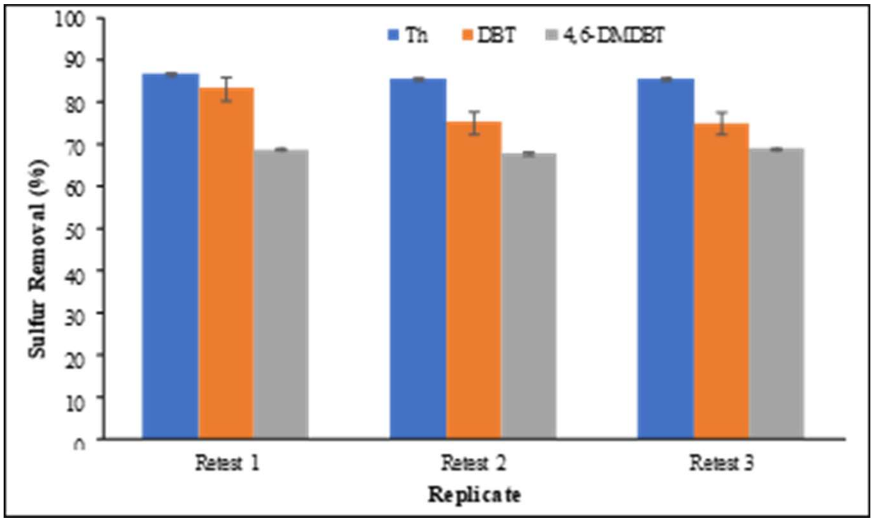

Figure 2. Repeatability test of Co/Fe- Al_2O_3 catalyst calcined at 400°C (Reaction conditions: Oxidant = TBHP, T = 50 °C, time = 30 min, solvent = DMF).

Catalyst recycling performance

The capacity of a catalyst to be recycled is crucial from an economic perspective [4]. Hence, 0.1g of Co/Fe-Al_2O_3 in the ratio of 10:90 catalyst calcined at 400 °C was tested for five consecutive cycles under similar conditions. The catalyst was retrieved, rinsed with methanol to reduce the adsorbed sulfur compound, and dried in an oven at 80 °C-100 °C for 12 hours and tested in the next cycle. It was found that there is no significant decline in activity even after three recycling runs as shown in (Figure 3). After the fourth and fifth cycle of the reaction, a decrease in the desulfurization activity of the catalyst were observed. This may relate to the washing or activation of some active catalyst spots during the oxidation or recycling process of the catalyst. A slight decrease in sulfur removal after the fourth cycle indicates that the active site was maintained during the reaction. In addition, the surface area of the used Co/Fe-Al_2O_3 catalyst (216 m^2/g) was very close to those of the fresh one (226 m^2/g) [21]. As a result, it was discovered that the Co/Fe-Al_2O_3 catalyst had a high catalytic activity for the Cat-ODS of diesel as well as a strong resistance to sulfur.

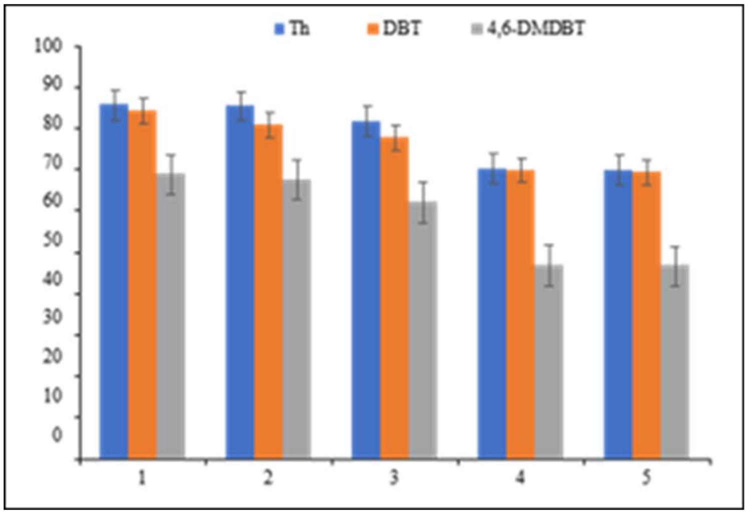

Figure 3. Catalyst cycling test of Co/Fe- Al_2O_3 catalyst calcined at 400 °C for 5 hours (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF)

Mechanistic study by computational

The mechanism of oxidative desulfurization with Co/Fe-Al_2O_3 catalyst in TBHP system was proposed in (Figure 4). Early research suggested that Fe^{3+}, O, and OH groups of iron oxides might engage with the thiophene ring, leading to adsorption through a variety of methodologies [26, 27]. The mechanism of the Co/Fe-Al_2O_3 catalyst include the formation of an intermediate product (1), as a consequence of the nucleophilic attack by TBHP on Co/Fe-Al_2O_3 surface when there is a reaction between TBHP and element Co or Fe. The electrophilic properties of peroxidic oxygen start to increase, made it more reactive because the electrons are extracted from the peroxyl moiety. DBT sulfoxide (3) is formed when DBT (2) is oxidised when responded to the nucleophilic attacks of sulfur in the DBT molecule (2) on the positively charged intermediate species (1). Following that, the DBT sulfoxide (3) was further oxidised to produce DBT sulfone (4) and tert-butanol (5) as by-products.

The energy level diagram for the oxidation of DBT and 4,6-DMDBT by TBHP in the presence of catalyst was displayed in (Figure 5). Several significant features were observed from the profile energy. Based on Table 3, the first oxidation of 4,6-DMDBT, -20.2 eV energy was released, higher than oxidation energy released by DBT which is -7.67 eV for the first step. Next, the second step of 4,6-DMDBT by adding oxygen to positively charge S atom demonstrated the releasing energy of about -1.65 eV. The energy required to form 4,6-DMDBT sulfoxide is 3.2 eV, which shown that is more energy required than DBT sulfoxide due to the presence of methyl group in the structure. The overall interaction energy between 4,6 DMDBT and catalyst is -23.19 eV which was less exothermic than DBT, -40.78 eV. The exothermic reactions indicate that sulfoxide and sulfone are persistent compounds. Based on the barrier heights in the reaction profile, we can see that the oxidation phase for sulfone synthesis was simpler than that of sulfoxide, and thus the sulfone product yield is expected to be greater than sulfoxide.

The bond length for Fe-O in 4,6-DMBT is 1.81 A°, a bit longer than the bond length in DBT (1.80 A°). Seeing as the methyl group was qualified to donate the aromatic ring the electrons, this suggests that the methyl group would impair the S-C strength qualities. Longer bond lengths on the scission of the S-C in ODS reaction may be easier in 4,6-DMDBT [28]. However, C-S bond cleavage was difficult to occur due to the steric hindrance effect of 4,6-DMDBT. On the contrary, according to conducted experiment, the ODS response in this reaction is simpler in DBT based on total energy. This is most likely due to the fact that DBT with access to the S-atom would result in a lower barrier height than the more sterically hindered S-containing 4,6-DMDBT molecule. Prove that methyl group steric hindrance was a key factor in the ODS system's selectivity.

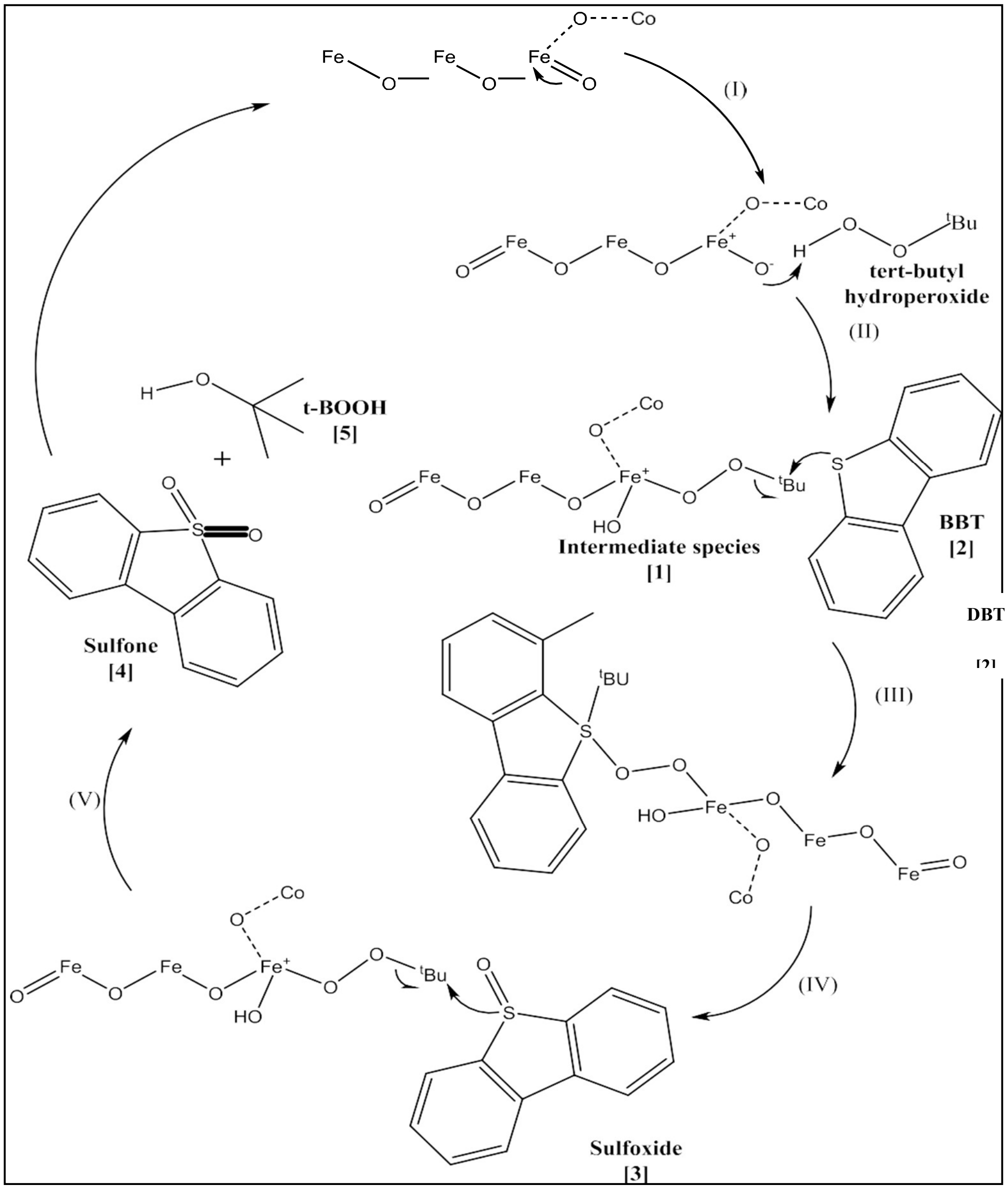

Figure 4. A proposed oxidation chemical route of dibenzothiophene by TBHP in the presence Co/Fe-Al_2O_3 catalyst

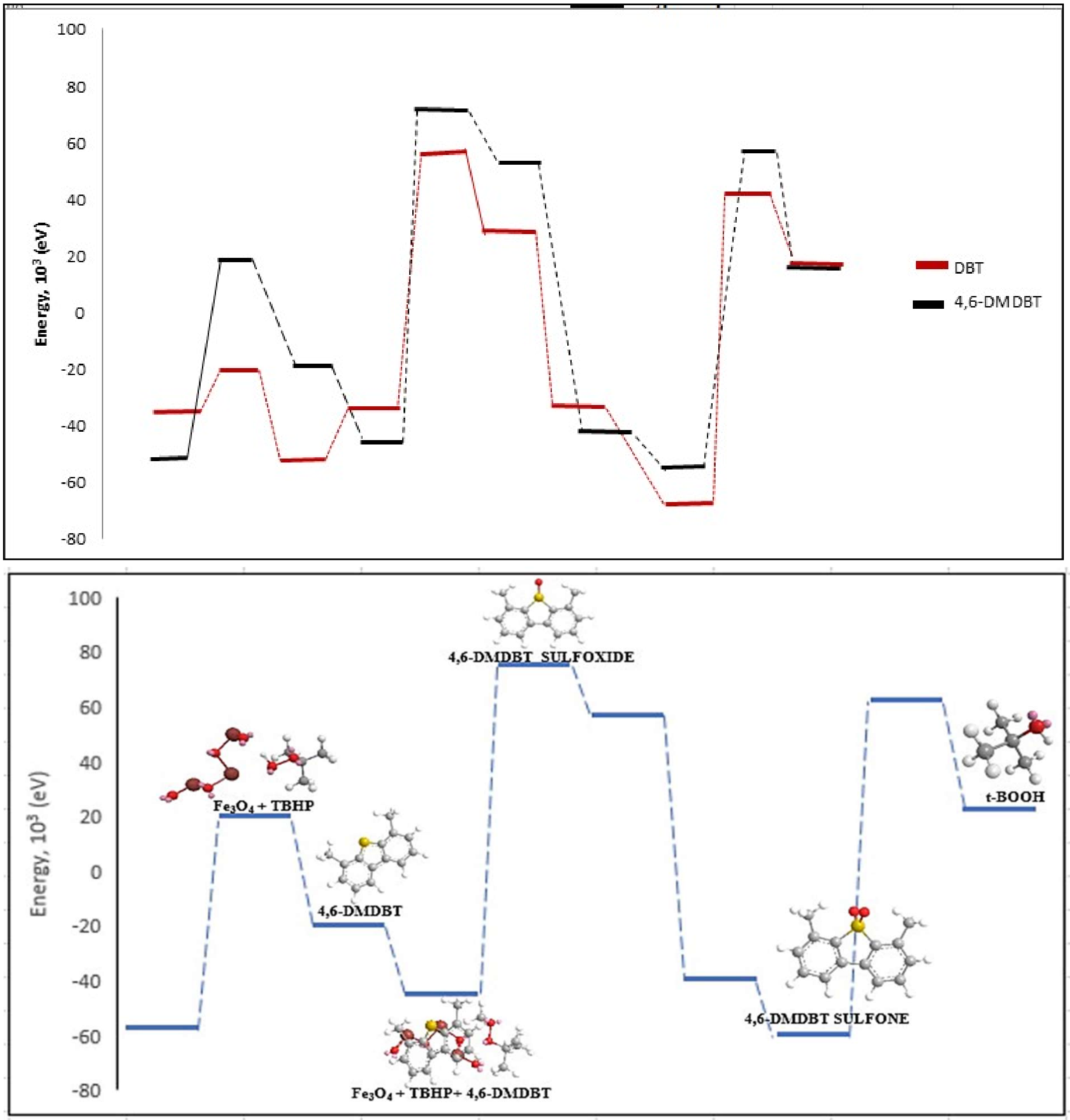

Figure 5. Energy level diagram for the oxidation of DBT and 4,6-DMDBT by TBHP in the presence of Co/Fe-Al_2O_3 catalyst

In order to determine the role of catalysts in oxidative desulfurization, an experiment was carried out in which the desulfurization process was examined without the use of a catalyst, as shown in (Figure 6). The first oxidation of DBT took place by nucleophilic attack of sulfur in DBT to oxygen in TBHP to form intermediate species. The energy required for the oxidation of DBT is 11.45 eV. This result showed that more energy was required to break the bond of reactant compared with oxidation of DBT in the presence of a catalyst. Next, the negatively charged oxygen in TBHP attacked hydrogen in intermediate to form tert-butanol and sulfoxide and the energy is released to -3.10 eV. Further reaction takes place by sulfoxide with TBHP to form sulfone and tert-butanol. The overall activation energy of the oxidation of DBT and TBHP without the presence of a catalyst is -4.01 eV.

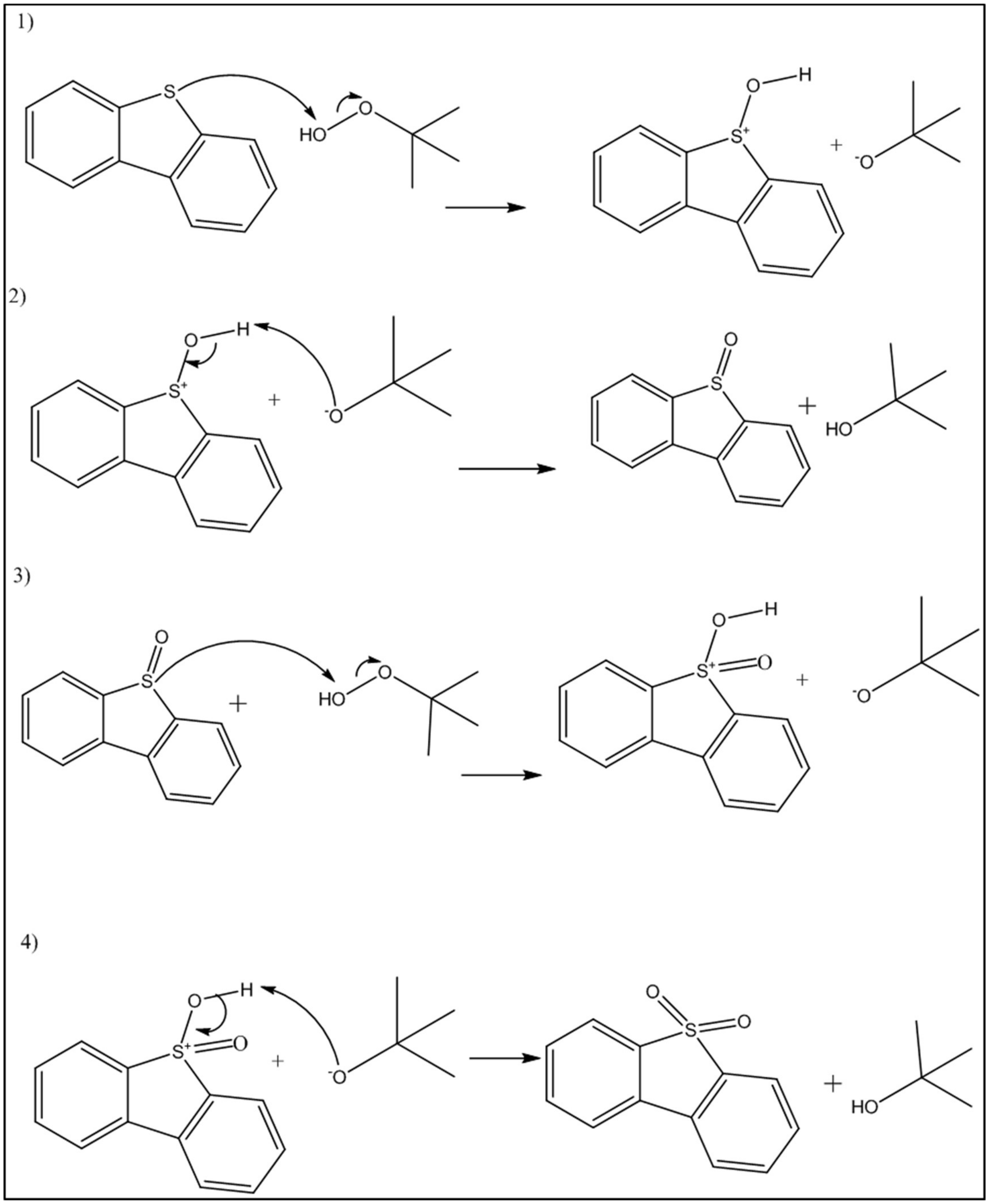

Figure 6. A proposed reaction for the oxidation of dibenzothiophene by TBHP

The activation energy in (Table 3), observed that the oxidation of DBT with catalyst released more energy than without a catalyst which is -40.78 eV and -4.01 eV. The energy profile demonstrated that all three reactions are exothermic. It shows that catalytic oxidation of DBT released more energy than uncatalyzed oxidation which is -40.78 eV and -4.01 eV, respectively. This result revealed that catalysts can have a major influence on ODS, which is consistent with the experimental studies. This had shown that by decreasing the activation energy for the reaction, the catalyst may accelerate the reaction.

Table 3. Reaction energy for the oxidation of DBT and 4.6-DMDBT by TBHP

Steps	**Ea(eV), x10^3**		
	DBT		**4,6-DMDBT**
	Without Catalyst	**With Catalyst**	**With Catalyst**
I	11.45	-7.67	-20.2
II	-3.10	0.83	-1.65
III	-3.26	-3.83	5.69
IV	-9.10	-12.03	3.2
V		-17.81	-10.23
Overall	-4.01	-40.78	-23.19

Conclusion

Co/Fe in the ratio of 10:90 catalyst calcined at 400°C showed the highest conversion of DBT at 100%, 4,6-DMDBT (79%), and thiophene (93%). Meanwhile, Co/Fe-Al_2O_3 catalyst could retrieve its catalytic recycling performance up to five cycles. The mechanism of 4,6-DMDBT by the proposed pathway was also investigated and found that higher activation energy -23.19 eV compared to DBT, and this agreed with the catalytic activity, where DBT is easy to remove compared to 4,6-DMDBT. Furthermore, the mechanism without the catalyst of DBT released lower energy, -4.01 eV respectively. In conclusion, the presence of the catalyst can speed up the reaction in removing sulfur compounds.

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