

Removal of dibenzothiophene from simulated petroleum by integrated γ -irradiation and Zr/alumina catalyst

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Abstract

Catalysts that can enhance the radiolytic decomposition of dibenzothiophene (DBT) in the simulated petroleum were identified. Among the tested catalysts, zirconium oxide impregnated on alumina (Zr/Al_2O_3) showed the highest catalytic activity in the presence of γ -rays irradiation. The preparation condition of the catalyst was optimized. The main factors that affected the conversion efficiency of DBT were studied. The results showed that in the presence of Zr/Al_2O_3 catalyst when the applied radiation dose was 179 kGy, the removal efficiency of DBT was 98.9%, an increase of over 80% compared to that without catalyst. The removal efficiency was higher with the lower dose rate at the same irradiation dose. The effect of γ -rays irradiation upon the structure of the catalyst was investigated by XRD, XPS and SEM techniques. The catalyst appeared to be stable under the γ -rays irradiation except the surface coverage by the oxidized organic compound. In addition, the possible mechanism for the synergistic effect of γ -rays irradiation and catalyst was proposed.

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Keywords: Dibenzothiophene; Petroleum; γ -Irradiation; Zr/Al_2O_3 catalyst

1. Introduction

Sulfur dioxide emitted from the combustion of fossil fuels is one of the key precursors of acid rain. Regulations on sulfur pollutants from fuel are becoming more stringent [1,2]. As a result, deep desulfurization to reduce sulfur contents in fuels to 15 ppmw (USA, 2006) and then to less than 10 ppmw is one of the most urgent issues in the petroleum industry [3–7].

There are many types of organic sulfur compounds present in the fuels, such as thiols, sulfide and heterocyclic sulfur. The conventional hydrodesulfurization (HDS) technology is highly efficient in removing thiols, sulfides and disulfides, but less effective for heterocyclic sulfur compounds such as benzothiophene, dibenzothiophene, and their alkylated derivatives [8–10]. A kinetic study shows that either the reactor volume or the catalytic activity must be at least three times larger than those currently used in refineries to be able to reduce the sulfur content of the diesel fuel from 500 to less than 15 ppmw using the current HDS technology [11–13]. Therefore, the development of an

alternative desulfurization technique has attracted more and more attention.

The attempts to apply γ -rays irradiation method to fuel processing have been performed for years [14–18]. This technology recognized as one of the green-chemical approaches can induce the valuable chemical reactions at room temperature under an atmospheric pressure. It has been observed that the inorganic sulfur could be removed from coal by γ -rays irradiation, although the demanded radiation dose was rather high. Recently, γ -irradiation has been proved to be an efficient method to removal thiol-sulfur from the simulated oil, and only several kGy was needed to obtain over 90% of the removal efficiency when some additives were used [19]. The γ -rays irradiation has been found to be able to decompose DBT in the simulated petroleum successfully in our previous study. However, the employed irradiation dosage was rather high to allow about 60% of the conversion efficiency [20]. In order to minimize the demanded irradiation dosage and improve the conversion efficiency, catalysts were used together with γ -radiation in this paper.

The effects of γ -rays radiation on the surface of some solid catalysts have been investigated, these studies were mainly focused on the pretreatment of the catalyst materials, such as

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doping [21–23]. The simultaneous utilization of the γ -rays radiation and catalyst to decompose DBT and its derivatives in the petroleum has never been studied.

2. Experimental

2.1. Reagents

The chemicals of DBT and dodecane were of chromatographic purity, which were purchased from Aldrich Corporation. The other chemicals, such as cobalt nitrate, zinc nitrate, were of analytical purity obtained from Shanghai Chemical Reagent Corporation. The particle size γ - Al_2O_3 particles was 100 meshes. The aeration gas was air and nitrogen. In this paper, the sample concentration of DBT was 500 ppmw.

2.2. Catalyst preparation

Catalysts were prepared by successive incipient wetness impregnation of γ - Al_2O_3 with an aqueous solution of metal nitrate. After each impregnation step the catalyst was dried in air at ambient temperature at 100 °C, and then was calcined within 673–873 K. In the preparation of the catalysts, the amount of the active component, calcination temperature and calcination time were varied. When the catalyst was used, sample was aerated by air or nitrogen to make the catalyst fully mixed with the liquid oil sample. The detail preparation conditions and character of catalysts are listed in Table 2.

2.3. Apparatus

The experimental setup employed was similar to that described previously [19]. ^{60}Co with the intensity of about 10^5 Ci was used as the radiation source of γ -rays. The range from 0.86 to 6.89 kGy/h of dose rate was used in this paper. The radiation dose (D , kGy) was calculated as follows:

$$D = Rt \quad (1)$$

where R (kGy/h) and t (h) mean the dose rate and the accumulating radiation time, respectively. The dose rate was dependent on the radial distance from the center of the source, which was calibrated regularly by Fricke Dosimetry method (GB193-89).

2.4. Analysis

Samples were analyzed with a GC-14B (Shimadzu, Japan), equipped with a flame photometric detector and capillary column (\varnothing 0.54 mm \times 30 m). For quantitative analysis, standard solutions of DBT were prepared for use to obtain the calibration curve. The removal efficiency of DBT, η , is calculated as follows:

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (2)$$

where C_0 and C represent the initial and final concentrations of DBT in dodecane solution before and after irradiated, respectively.

The products from the decomposition of DBT and dodecane after the irradiation were identified with GC/MS (Shimadzu, P2010).

2.5. Catalyst characterization

The surface area of the catalyst was measured via BET Method using Micromeritics apparatus. Surface areas and average pore diameters are presented in Table 2. The surface topography was observed by scanning electron microscopy (S-2150, HITACHI). X-ray powder diffraction (XRD) was used to characterize the catalysts. Data were collected on a Shimadzu powder diffractometer system using Cu $K\alpha$ radiation (40 kV, 40 mA). Typically, the diffractograms were obtained from 10 to 80° 2θ with a step size of 0.02°. The count time was 1 s over each step. The X-ray photoelectron spectroscopy analysis was carried out with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and a Mg $K\alpha$ 120 W X-ray source. The binding energies (BE) were referenced to the C_{1s} line at 291.9 eV.

3. Results and discussions

3.1. Catalyst selection

Six solid powders were evaluated as catalysts for the efficiency (Table 1). Alumina (Al_2O_3) was used both as the catalyst and the carrier of other active components (metal oxides). The loading content of Mn, Co, Zn and Zr on Al_2O_3 was about 10 wt.% in the form of their respective oxides, and TiO_2 was of chemical purity in powder (about 100 meshes). The volume ratio of the catalyst to oil, C/O, was about 0.1 g/ml.

Table 1
The removal efficiency of DBT with various catalysts under different conditions

Condition	Catalysts					
	Al_2O_3	Al_2O_3 -Mn	Al_2O_3 -Co	TiO_2	Al_2O_3 -Zn	Al_2O_3 -Zr
Catalyst without radiation	11.2%	4.8%	3.8%	5.7%	5.1%	8.9%
Catalyst with radiation	17.6%	29.28%	66.8%	18.4%	25.7%	98.9%
Radiation without catalyst	15.2%					

The radiation dose was 179.1 kGy (with dose rate of 3.85 kGy/h) if γ -radiation was involved; all the tests were performed with aeration of air at 298 ± 2 K. The flow rate of air was about 30 ml/min. The loading content of every metal oxides on Al_2O_3 were all about 10%, and all the catalysts were calcined at 673 K for 2 h. The ratios of the employed catalyst amount to the simulated oil volume, C/O, were all about 0.1 g/ml.

Also, the removal efficiencies of DBT by the adsorption on solid catalysts (without irradiation) and by γ -rays radiation were listed in Table 1 for comparison.

As shown in Table 1, about 10% of DBT in the oil was adsorbed by alumina without irradiation. However, DBT adsorption capacity on Al_2O_3 decreased when γ - Al_2O_3 was impregnated with metal oxides. And about 8.9% of DBT was adsorbed on $\text{Zr}/\text{Al}_2\text{O}_3$.

When γ -irradiation was applied in the presence of the catalysts, different effect on the removal of DBT was observed. Alumina improved only slightly the removal of DBT. $\text{Mn}/\text{Al}_2\text{O}_3$, TiO_2 and $\text{Zn}/\text{Al}_2\text{O}_3$ catalysts exhibited a detectable improvement to the removal of DBT, but their effect was small if the contribution from the adsorption was taken account. However, $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Zr}/\text{Al}_2\text{O}_3$ displayed significant catalysis to the removal of DBT in the presence of radiation. The removal efficiency of DBT increased from 15.2% to 66.8% and 99.1% when $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Zr}/\text{Al}_2\text{O}_3$ was employed, respectively. Therefore, the further and detailed study was focused on $\text{Zr}/\text{Al}_2\text{O}_3$ catalyst in this paper.

3.2. Determination of the catalyst preparation method

3.2.1. The content of the active component in catalysts

Fig. 1 shows that the catalytic activity or DBT removal efficiency, η , increased from 40.7% to 99.1% with the increase of the loading amount from 2 to 15 wt.% at a radiation dose of 179.1 kGy. However, the pace of the increase slowed down beyond a Zr oxide loading of 10 wt.%. Apparently there is a limitation on the catalytic activities with increasing Zr oxide content. Overloading of Zr oxide on Al_2O_3 could result in the deterioration of catalyst surface, such as the agglomeration of the Zr oxide and the excessive loss of the surface area. In addition, the cost of the catalyst increases with the increase of the loading of Zr. The optimal content of Zr oxide on Al_2O_3 appeared to be about 10% considering the cost and catalytic effectiveness of the catalyst.

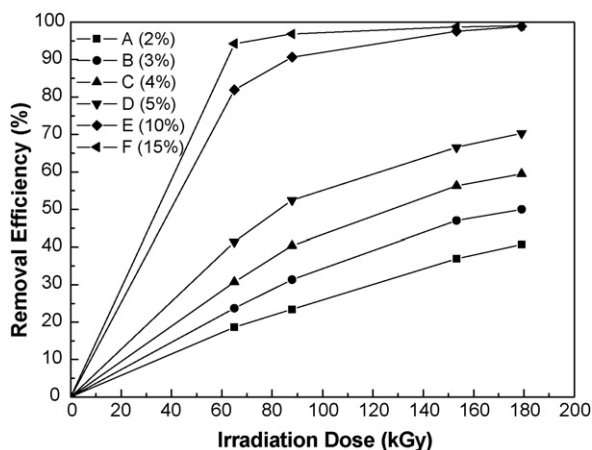


Fig. 1. Zr oxide loading content on the catalyst vs. DBT removal efficiency. Radiation dose rate was 3.85 kGy/h at 298 ± 2 K. The initial concentration of DBT was 0.5 g/l. The flow rate of air was about 30 ml/min. The ratio of the employed catalyst amount ($\text{Zr}/\text{Al}_2\text{O}_3$, 100 mesh) to the simulated oil volume, C/O, was 0.1 g/ml. The catalyst was calcined at 673 K for 2 h.

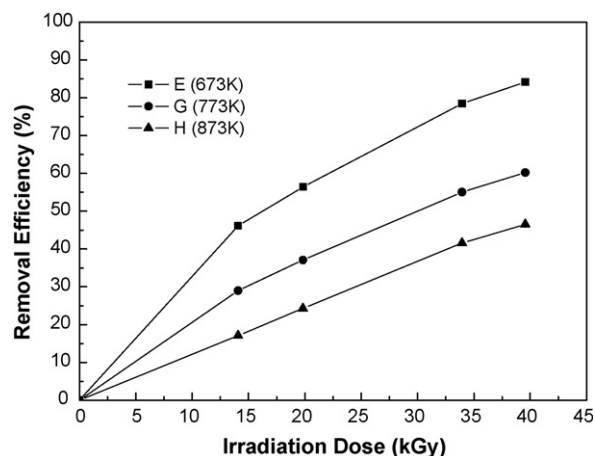


Fig. 2. DBT removal efficiency with the catalysts at different calcination temperature. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K, and the initial concentration of DBT was 0.5 g/l; radiation dose rate was 0.86 kGy/h. The flow rate of air was about 30 ml/min. The ratio of the employed catalyst amount ($\text{Zr}/\text{Al}_2\text{O}_3$, 100 mesh) to the simulated oil volume, C/O, was 0.1 g/ml. The catalyst was calcined for 2 h.

3.2.2. Calcination temperature

It is known that calcination temperature is a key factor in the preparation of catalysts. The purpose of calcination is to convert the active component (Zr nitrate) to the demanded speciation (Zr oxide). Fig. 2 shows the effect of calcination temperature on the activity of catalyst. The results indicated that the removal efficiency of DBT was 84.1% when the calcination temperature was 673 K with the radiation dose of 39.6 kGy. However, it dropped to 60.2% and 46.5% when calcination temperature increased to 773 and 873 K, respectively. According to the above result, the suitable calcination temperature seemed to be around 673 K.

3.2.3. Calcination time

Besides calcination temperature, the calcination time can also affect the catalytic activity. Fig. 3 shows that the removal

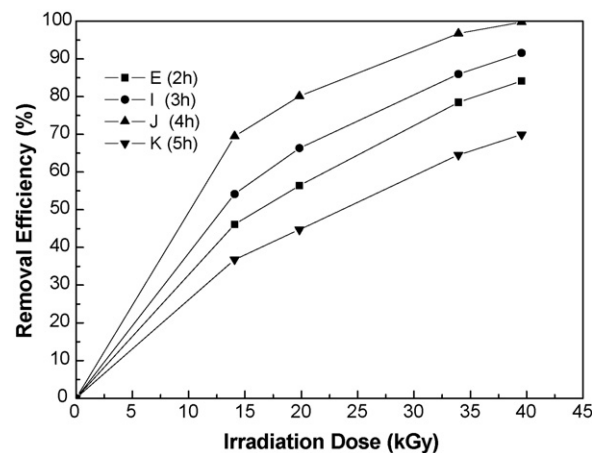


Fig. 3. DBT removal efficiency with the catalysts at different calcination time. DBT was dissolved in dodecane and irradiated at 298 ± 2 K, and the initial concentration of DBT was 0.5 g/l; radiation dose rate was 0.86 kGy/h. The flow rate of air was about 30 ml/min. The ratio of the employed catalyst amount ($\text{Zr}/\text{Al}_2\text{O}_3$, 100 mesh) to the simulated oil volume, C/O, was 0.1 g/ml. The catalyst was calcined at 673 K.

Table 2
The preparation conditions and BET surface area of catalysts and catalytic activities

ZrO ₂ loading amount (wt.%)	Calcination temperature (K)	Calcination time (h)	Specific surface areas (m ² /g)	Average pore diameter (nm)	DBT removal efficiency ^a (%)
10	673	2	230.15	7.17	84.1
10	773	2	218.06	7.09	60.2
10	873	2	181.17	7.19	46.5
10	673	3	239.27	7.10	91.6
10	673	4	248.57	7.13	99.8
10	673	5	214.47	7.14	69.9

Zr oxide was impregnated on alumina particles of 100 meshes.

^a The radiation dose was 39.6 kGy, and the ratios of the employed catalyst amount to the simulated oil volume, C/O, were all about 0.1 g/ml.

efficiency was 84.1% when the calcination time was 2 h with the radiation dose of 39.6 kGy. It reached to 91.6% and 99.8% as the calcination time was 3 and 4 h, respectively, but fell to 69.9% when the calcination time increased to 5 h.

In order to explicate the effect of calcination temperature and time on the surface structure of catalyst, the BET surface area of catalysts from different preparation conditions were measured (Table 2). It can be seen that the surface area of catalysts changed when the preparation condition was different, and the BET surface area dropped when the calcination temperature or time was too high or too long. The specific activity of catalyst was related to the surface area. Also the calcination condition could affect the catalytic activity of the catalyst.

3.3. Effect of irradiation parameters and environment

3.3.1. Radiation dose and dose rate

It was found that the removal efficiency of DBT increased with the increase of the radiation dose (Figs. 1–3). In order to study the effect of radiation dose rate, DBT was irradiated at different radiation dose rate in the presence of catalyst. The depletion of DBT concentration with radiation dose is shown in Fig. 4, in which three dose rates were utilized. It was obvious that the removal efficiency was larger at the same radiation dose

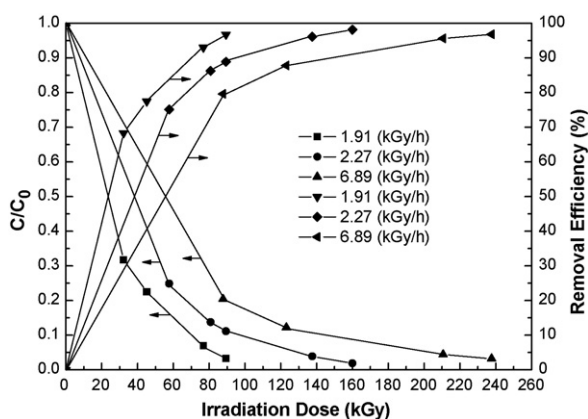


Fig. 4. Effect of radiation dose and dose rate on the removal efficiency of DBT or the depletion of DBT concentration. DBT was dissolved in dodecane and irradiated at 298 ± 2 K, and the initial concentration of DBT was 0.5 g/l; the flow rate of air was about 30 ml/min. The ratio of the employed catalyst amount (Zr/Al₂O₃, 100 mesh) to the simulated oil volume, C/O, was 0.1 g/ml. The catalyst was calcined at 673 K for 2 h.

when the radiation dose rate was lower. To obtain a 98% removal efficiency, the radiation doses needed were 89.6, 137.5 and 237.7 kGy for the radiation dose rate of 1.91, 2.77 and 6.89 kGy/h, respectively. This trend was reverse in the case without catalysts, where the higher dose rate gave rise to higher removal efficiency at the same dose [20]. This difference could be explained as follows. DBT is made up of conjugated π -bond and the π electrons in DBT molecule are non-localized, so it is very stable in its molecular structure. When DBT was irradiated by a single γ -photon, the energy absorbed by DBT molecule would be distributed evenly and quickly in the whole molecule. In this case, π electron in the targeted molecule will transfer from its high excitation state to low excitation state or the ground state. This phenomenon is known as radiation protection. Therefore, DBT would not be converted effectively in the low excitation state. However, when the density of γ -photons was thicker at the higher radiation dose rate, the excitation time interval for the target-molecule by two series γ -photons was so short that the first excitation still remained before the second γ -photon's excitation occurred, and two excitation processes were overlapped. In this case, the conversion of DBT should be more efficient.

When the catalyst was involved, the depletion mechanism of DBT on catalyst surface was different. The adsorbed DBT on the catalyst was supposed to be excited and converted more easily, and other reactive species would be produced on the catalyst surface under γ -rays radiation. In this case, the conversion rate of DBT was determined by the adsorption step, the radiation dose rate and the catalytic activity of the surface simultaneously. Therefore, the depletion rate was not positively dependent on the dose rate in the presence of catalyst.

3.3.2. Aeration with nitrogen or air

The influence of aeration with nitrogen and air (with about 21% of oxygen and 79% nitrogen) on the radiation removal of DBT in the presence of catalyst is illustrated in Fig. 5. It can be seen that the removal efficiency with the aeration of nitrogen was almost the same as that without aeration. However, the aeration of air displayed stimulation on the removal of DBT in the presence of catalyst. When the radiation dose was 179.1 kGy, the removal efficiency was about 60.5% and 67.6% for the static radiation and the aeration of nitrogen, respectively, but it increased to above 98.9% when air was introduced to the solution. This phenomenon was also different from that without

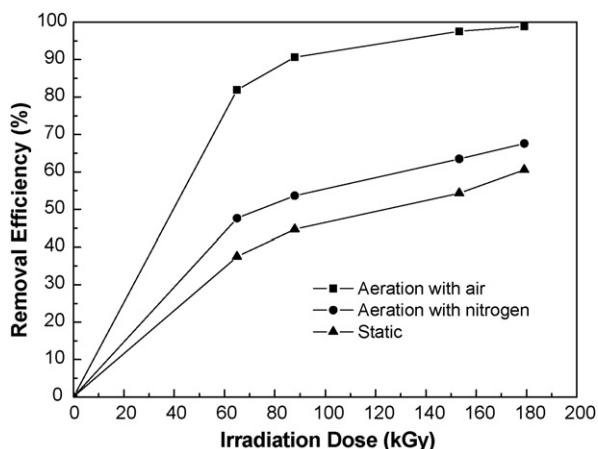
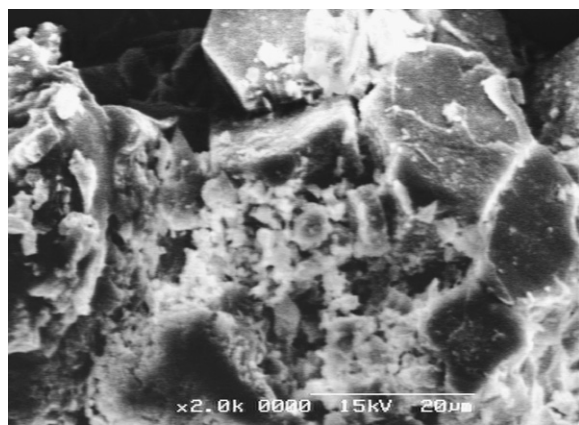
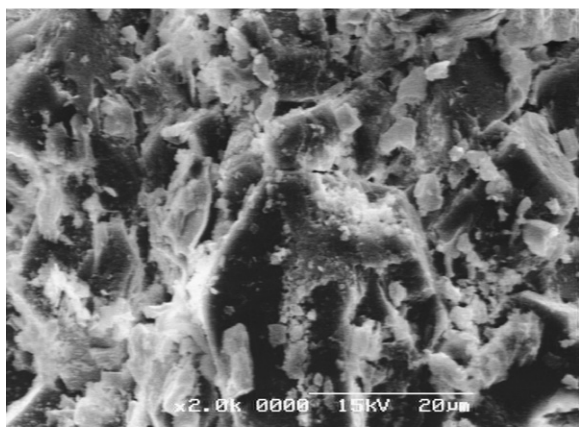


Fig. 5. DBT removal efficiency vs. radiation dose with different aeration conditions. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K, and the initial concentration of DBT was 0.5 g/l; radiation dose rate was 3.85 kGy/h. The flow rate of nitrogen or air was about 30 ml/min. The Zr oxide loading content was 10%, and the catalyst was calcined at 673 K for 2 h. The ratio of the employed catalyst amount ($\text{Zr}/\text{Al}_2\text{O}_3$, 100 mesh) to the simulated oil volume, C/O, was 0.1 g/ml.



(a) Before irradiated



(b) After irradiated

Fig. 6. SEM picture of catalyst before and after irradiated. The Zr oxide loading content was 10%, and the catalyst was calcined at 673 K for 2 h. The irradiation dose was 179.1 kGy.

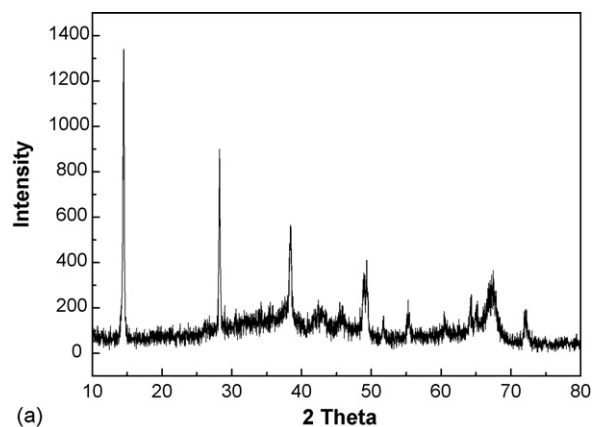
catalyst, where the aeration of oxygen displayed significant inhibition to the conversion of DBT [20].

These results suggested that the radiation conversion of DBT by in the homogeneous liquid phase was not by way of the oxidation reaction mechanism. It appeared that oxygen would eliminated some reactive species that were useful for the conversion of DBT. On the contrary, oxygen was helpful to the depletion of DBT in the presence of catalyst, and the catalytic oxidation in the presence of oxygen appeared to be more effective under γ -radiation surroundings.

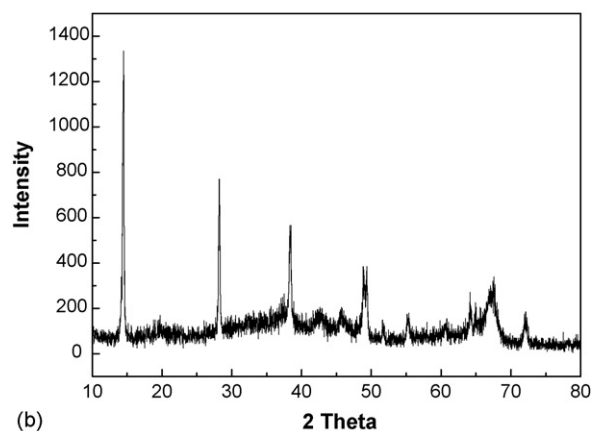
3.4. Structure and activity stability of the catalyst under γ -rays radiation

The morphology of the $\text{Zr}/\text{Al}_2\text{O}_3$ catalyst was probed by Scanning Electron Microscopy technique (SEM), and was found that the surface appearance of the catalyst did not show detectable difference before and after irradiation (Fig. 6).

The X-ray diffraction technique (XRD) images of the catalyst before and after irradiation are shown in Fig. 7. The characteristic peak of Zr oxide could not be distinguished clearly in the figures because of its low content and amorphous status. Nevertheless, the XRD images of the catalyst were not changed before and after the radiation. Therefore, the indication from the SEM and XRD measurements is that γ -rays



(a)



(b)

Fig. 7. The XRD patterns of the catalysts before irradiated (a) and after irradiated (b). The Zr oxide loading content was 10%, and the catalyst was calcined at 673 K for 2 h. The irradiation dose was 179.1 kGy.

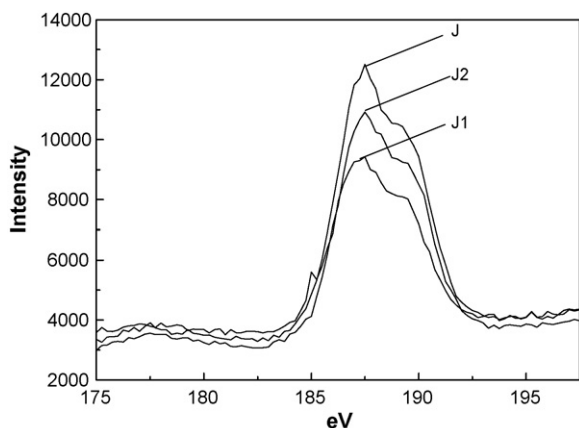


Fig. 8. XPS spectrum of Zr oxide in catalyst. The Zr oxide loading content was 10%, and the catalyst was calcined at 673 K for 2 h. The irradiation dose was 179.1 kGy for this figure. J represented the fresh catalyst; J₁ was the catalyst which has been used for 90 h. J₂ was the regenerated catalyst from J₁ by calcination at 673 K.

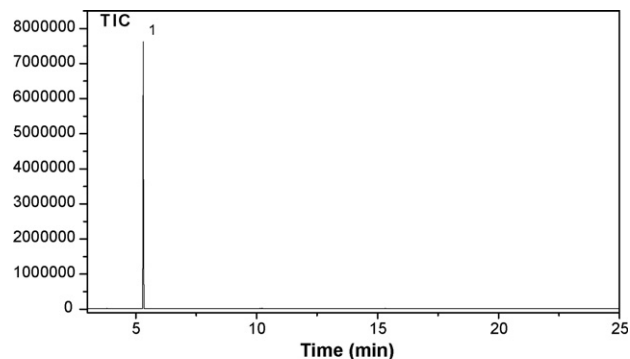
did not affect the surface structure and crystal structure of the catalyst under the test conditions employed.

The binding energy of Zr in the fresh and irradiated catalysts was identical as determined by the XPS spectroscopy (Fig. 8), which indicated that the valence of Zr was not changed by the radiation. However, the binding adsorption intensity of Zr became weaker when the catalyst worked in the irradiated petroleum for a period of time, and the binding adsorption intensity of carbon increased as well. In this case, the activity of catalyst also dropped markedly. The removal efficiency of DBT with the fresh catalyst was 98.9% with the irradiation dose of 179.1 kGy. However, it was only 57.8% for the recycled catalyst without regeneration. When the recycled catalyst was thermally regenerated at 673 K and reused, the removal efficiency of DBT reached 95.6%, which was near to that of the fresh catalyst. Apparently the oxidized organic matter from the decomposition of DBT and dodecane can be strongly adsorbed on the catalyst surface, and this process was irreversible. The catalytic activity would decrease when most of the active sites on the catalyst surface were covered by the adsorbed compounds. Therefore, the key to maintain the sustainable catalysis is to minimize the irreversible adsorption of the oxidized organic byproducts on the catalyst.

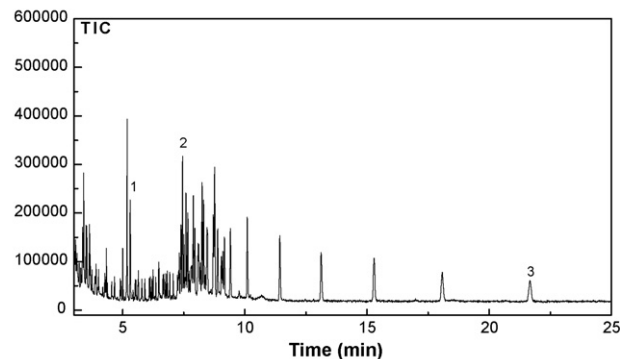
3.5. The conversion products of DBT and dodecane

The conversion products of DBT were identified by GC/MS techniques (Fig. 9). The main decomposition product of DBT was dibenzothiophene sulfone ($C_{12}H_8SO_2$). A small amount of disulfide ($C_{24}H_{50}S_2$) was also detected. Meanwhile, the extracted products with methanol from the used catalyst were also analyzed by GC/MS, and the main products which presented in the irradiation solution (Fig. 9b) and were adsorbed on the catalyst surface (Fig. 9c) were consistent.

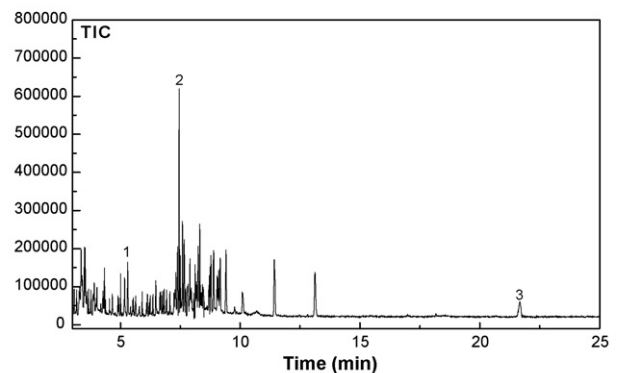
In order to evaluate the side effect of γ -irradiation on hydrocarbon in petroleum, the degradation products of dodecane were also identified. Some oxidation derivatives of dodecane were identified in the samples irradiated when



(a) before irradiated



(b) after irradiated (liquid phase)



(c) after irradiated (Extraction liquid from the used catalyst)

Fig. 9. GC/MS spectrum of DBT before irradiated (a) and after irradiated (b) in the presence of Zr/Al₂O₃, respectively. The peak 1 represents DBT, the peak 2 represents dibenzothiophene sulfone ($C_{12}H_8SO_2$), and the peak 3 represents disulfide ($C_{24}H_{50}S_2$). The radiation dose rate was 3.85 kGy/h and radiation dose was 179.1 kGy. The peak intensity in (b) and (c) were magnified 13 and 10 times compared with that in (a), and most of the other peaks in (b) and (c) were the oxygen-containing derivatives of dodecane.

oxygen was present. The main products were dodecanol, dodecyl ketone, and dodecyl aldehyde. The result of semi-quantitative analysis by GC showed that the degradation of dodecane was very slow and the total concentration of the oxidation species was about 1.2% even though oxygen was abundant, which meant that the radiation had less destructive effect on the main components of petroleum.

Since dibenzothiophene sulfone and disulfide can be easily removed from oil than DBT by conventional technologies, the treatment with the radiation should be useful for the pre-desulfurization of DBT.

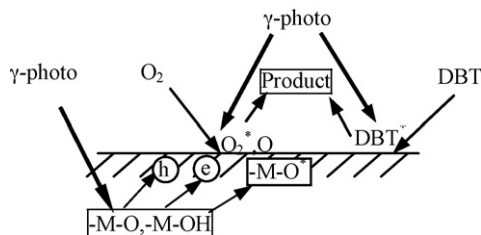
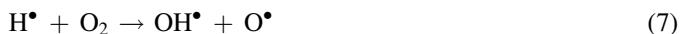
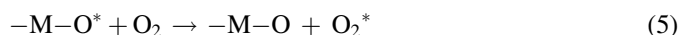
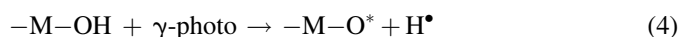
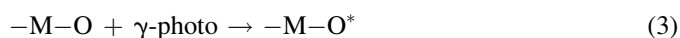


Fig. 10. The proposed mechanism scheme for the cooperation of catalyst and γ -rays. \oplus and \ominus refers the excited electron-hole pairs on the catalyst. The superscript * refers the excited state species.

3.6. Discussion on the catalysis mechanism

The possible reaction mechanisms for the DBT removal were proposed as follows. DBT was firstly adsorbed rapidly on the catalyst surface through physical adsorption. Then, the adsorbed DBT on the catalyst was excited by γ -photons. At the same time, oxygen would form reactive species, such as the excited oxygen (O_2^*), oxygen atom, and OH radicals by γ -rays radiation. Meanwhile the lattice-bound oxygen atom in oxide might also be activated. Therefore, the oxygen atom for DBT oxidation might be from either excited oxygen molecule or the lattice-bound oxygen atom in the catalyst. The step-by-step reactions are illustrated in Fig. 10.

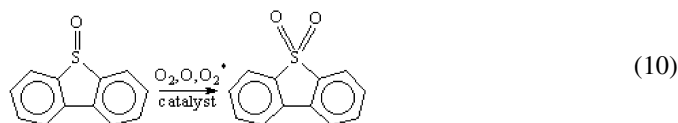
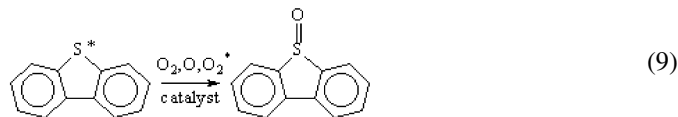
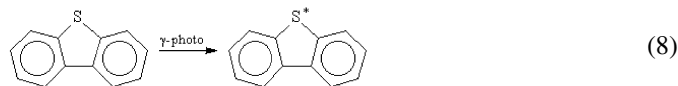
The solid catalyst Zr/Al_2O_3 is composed of $-M-OH$ and $-M-O$ bands (M referred to metal ions, such as Zr or Al), which would result in charge separation when they adsorbed γ -rays, a behavior similar to that of semiconductor particles under UV or visible irradiation [24,25]. γ -Photons were energetic enough to create electron-hole pairs in oxide particles, most of which recombine within few picoseconds to produce triplet excitons. Similar study [26] has indicated that both triplet excitons and trapped electrons can react with surface-bound OH groups to generate H-atoms, which can subsequently react with oxygen to produce OH radicals. Also, holes would react with H-atoms and surface-bound hydroxyl defects in the oxide layer to form surface-bound protons and OH radicals, respectively. In addition, the lattice oxygens, $-M-O$, could be excited into $-M-O^*$ and even formed surface-bound oxygen atom. Eqs. (3)–(7) can be used to describe the formation of the reactive species:



where $-M-OH$ and $-M-O$ refer to hydroxide band and O band bound to a metal oxide surface. While the importance of holes is not exactly known, one would expect them to generate OH radicals by reacting with surface hydroxyl groups or to be scavenged by H-atoms to produce lattice-bound protons [25].

The surface-adsorbed DBT species may directly interact with the oxygen atom and OH radicals through series of

oxidation processes. Meanwhile, DBT adsorbed on the catalyst surface can also be excited by γ -photon, and the physical adsorption was converted to chemisorbed. The chemisorbed and excited DBT was supposed to be oxidized more easily by reacting with oxygen species or OH radicals. The main oxidation processes of DBT are illustrated with Eqs. (8)–(10):



From the GC-MS result, dodecane disulfide ($C_{24}H_{50}S_2$) was another detectable byproduct for DBT conversion, which indicated that some sulfur atoms in DBT molecules were detached from the aromatic rings. The detached sulfur then was converted to disulfide compounds through the reaction with dodecane under γ -rays radiation.

4. Conclusion

Catalysts were employed to promote the radiolytic conversion of dibenzothiophene (DBT). Among the tested catalysts, Zr/Al_2O_3 showed the best performance to the oxidation of DBT in the presence of γ -rays irradiation. The preparation condition of the catalyst, such as the loading content, calcinations temperature and time, was optimized. The results showed that in the presence of Zr/Al_2O_3 when the radiation dose was 179 kGy, the removal efficiency of DBT was about 98.9%, an increase of 80% compared to that without catalyst. The removal efficiency at the same irradiation dose appeared to be larger with the lower dose rate. The catalyst appeared to be stable under the γ -rays irradiation except the surface coverage by the oxidized organic compounds. The possible mechanism for the synergistic effect of the γ -rays irradiation and catalyst was proposed.

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