

Deep desulfurization of diesel fuels by catalytic oxidation

YU Guoxian, CHEN Hui, LU Shanxiang (✉), ZHU Zhongnan

School of Chemical Engineering, East China University of Science & Technology, Shanghai 200237, China

© Higher Education Press and Springer-Verlag 2007

Abstract Reaction feed was prepared by dissolving dibenzothiophene (DBT), which was selected as a model organosulfur compound in diesel fuels, in *n*-octane. The oxidant was a 30 wt-% aqueous solution of hydrogen peroxide. Catalytic performance of the activated carbons with saturation adsorption of DBT was investigated in the presence of formic acid. In addition, the effects of activated carbon dosage, formic acid concentration, initial concentration of hydrogen peroxide, initial concentration of DBT and reaction temperature on the oxidation of DBT were investigated. Experimental results indicated that performic acid and the hydroxyl radicals produced are coupled to oxidize DBT with a conversion ratio of 100%. Catalytic performance of the combination of activated carbon and formic acid is higher than that of only formic acid. The concentration of formic acid, activated carbon dosage, initial concentration of hydrogen peroxide and reaction temperature affect the oxidative removal of DBT. The higher the initial concentration of DBT in the *n*-octane solution, the more difficult the deep desulfurization by oxidation is.

Keywords activated carbon, formic acid, H₂O₂, dibenzothiophene, oxidative desulfurization

1 Introduction

Although deep hydrodesulfurization is playing a leading role in clean fuel technologies, oxidative desulfurization (ODS) has received more and more attention as a new method for deep desulfurization of light oil [1,2]. Various studies on the ODS process using different oxidizing systems such as acetic acid-H₂O₂ [1], formic acid-H₂O₂ [2], plasma [3], and so on, have been reported. It is known to all that carbon materials not only act as catalysts in a lot of redox reactions [4,5] but also act as adsorbents [6,7]. Hydroxyl radicals generated from hydrogen peroxide result in the oxidation of dibenzothiophene to form SO₄²⁻ [8,9], and activated carbon

(AC) can catalyze hydrogen peroxide to produce hydroxyl radicals when pH is less than 7.0. It is not reported that whether hydrogen peroxide, when catalyzed by activated carbon-formic acid, can produce hydroxyl radicals and performic acid to effectively oxidize thiophenic organic sulfides. Oxidative removal of dibenzothiophene (DBT) in *n*-octane with hydrogen peroxide catalyzed by activated carbon-formic acid was mainly investigated in this paper. Dibenzothiophene, which was selected as a model organosulfur compound in diesel fuels, was dissolved in *n*-octane. The catalytic performance of activated carbons with saturation adsorption of DBT was investigated in the presence of formic acid. In addition, the effects of activated carbon dosage, formic acid concentration, initial concentration of hydrogen peroxide, initial concentration of DBT and reaction temperature on the oxidation of DBT were investigated.

2 Experimental

2.1 Materials and apparatus

Hydrogen peroxide (30 wt-%, analysis purity reagents – AR) was obtained from Shanghai Pengpu Chemicals. Dibenzothiophene (AR) was obtained from ACROS Organics. Formic acid (AR) and *n*-octane (chemical purity reagents – CP) were obtained from Shanghai Lingfeng Chemicals. Carbon-φ3.0 is granular coal-based, steam-activated carbon (sieved into 40–60 mesh, ferric salt content less than 0.2 wt-%). W602 and W660 are powdered wood-based, phosphoric acid-activated carbons (80–100 mesh, ferric salt content less than 0.1 wt-%). All the activated carbons in this study were obtained from the Shanghai Activated Carbon Co. The carbons were repeatedly washed with deionized water till the pH of the filtrate was the same as that of water, and then dried in an air oven at 120°C for 12 h.

2.2 Tissue characterization of activated carbon

An automated adsorption apparatus (Micromeritics, ASAP2010) was used to determine the specific surface areas

and pore volumes (BJH (Barrett-Joyner-halenda) method) by N_2 adsorption. The adsorption measurements were performed at the liquid N_2 temperature (77 K). Structural parameters of the selected activated carbons are shown in Table 1.

Table 1 Structural parameters of the selected activated carbons

Sample	BET surface area / $m^2 \cdot g^{-1}$	Total pore volume / $cm^3 \cdot g^{-1}$	Micropore volume / $cm^3 \cdot g^{-1}$	Average pore diameter /nm
660	2115	1.284	0.244	3.05
602	2007	1.177	0.284	2.96
$\phi 3.0$	1496	0.738	0.440	2.49

2.3 Experimental method

2.3.1 Catalytic test of activated carbons under saturation adsorption

The catalytic oxidation procedure was as follows: the first step, 36 mL of *n*-octane solution containing DBT (initial sulfur concentration $0.556 \text{ g} \cdot \text{L}^{-1}$) and 0.3 g of activated carbon were added to a flat bottom flask. The mixture was stirred continuously at 25°C for 12 h, and then filtrated to obtain the carbon adsorbing DBT. In the second step, a 100 mL three-necked flask, fitted with a condenser, a mechanical stirrer and a thermometer, was used to perform the oxidation reaction. The reaction flask was immersed in a thermostatically controlled (within $\pm 1^\circ\text{C}$) water bath to carry out the reactions at 60°C . 36 mL of *n*-octane solution containing DBT and 0.3 g of the carbon adsorbing DBT were introduced to the flask. 30 wt-% H_2O_2 solution, deionized water and formic acid were introduced to a 20 mL beaker, with the aqueous volume at 9 mL. The aqueous mixture was transferred to the reaction flask once the *n*-octane solution was heated to 60°C . After the reaction mixture was kept at 60°C for 60 min and continuously stirred at 750 r/min, the oil phase was separated to analyze DBT content. Conversion of DBT was calculated as follows

$$y = [(C_0 - C_1) / C_0] \times 100\%$$

where C_0 is the initial concentration of sulfur in the *n*-octane solution, C_1 is the sulfur concentration of the filtrate when the reaction was over.

2.3.2 Oxidation of dibenzothiophene

The typical procedure was as follows: 36 mL of *n*-octane solution containing DBT and activated carbon were added to a 250 mL four-necked flask, fitted with a condenser, a mechanical stirrer and a thermometer. 30 wt-% H_2O_2 solution, deionized water and formic acid were transferred to the reaction flask once the *n*-octane solution containing DBT was heated to a designated temperature. The aqueous phase volume was 9 mL.

2.4 Analysis method

Sulfur content was analyzed by GC920-FPD (gas chromatography with a capillary column (HP-5) using a flame

photometric detector (FPD)). The FPD detect limit was $5 \times 10^{-12} \text{ g S/S}$ (sulfur in lauryl mercaptan), and the FPD max sensitivity was $1 \times 10^{-10} \text{ A/mA}$.

Aqueous products of oxidation of DBT were identified as follows. First, DBT sulfone synthesized according to Reference [2] was used to identify the residence time in GC-FPD chromatogram map. In the second step, oxidation of DBT was carried out with hydrogen peroxide catalyzed by AC-HCOOH, and then AC was leached and washed three times with 10 mL deionized water every time, and then a mixture was obtained by mixing the wash water and the separated aqueous mixture; DBT sulfone in the resulting mixture was identified by GC-FPD, and the SO_4^{2-} ion was identified by adding BaCl_2 into the resulting aqueous mixture, which produced a white precipitate. In the third step, the oxidation of DBT was carried out with hydrogen peroxide catalyzed by only AC, and then analysis procedure was the same as the second step, only SO_4^{2-} ion was identified.

3 Results and discussion

3.1 Selection of activated carbon catalyst

Hydroxyl radicals, which are strong oxidizing agents, can be produced on the carbon surfaces when carbon materials, such as activated carbon and carbon black, react with organic peroxides or inorganic peroxides [10]. Donnet [11] pointed out that solid carbon materials can catalyze peroxides to decompose into radicals, and he determined the amount of the radicals under special conditions. Activated carbon can catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals, and the short life radicals produced during the surface reactions are likely to be resonance-stabilized on the carbon surfaces [10]. Firth and Watson [12] found that activated carbon contains a lot of metals such as Pt, Ag and Pb, metal ions such as Fe^{3+} , Cr^{3+} , Cu^{2+} and Ag^+ , and metal oxides such as MnO_2 and Fe_2O_3 , which can catalyze hydrogen peroxide to produce free radicals with very high oxidation potential (OH^\cdot and HO_2^\cdot).

In order to obtain the truly catalytic performance of the carbons in the oxidative removal of DBT by hydrogen peroxide, the adsorptive removal of DBT must be eliminated. Therefore, before the activated carbons were introduced into the reaction system, they were thoroughly saturated with DBT by being immersed into an *n*-octane solution containing DBT for 12 h. Figure 1 shows the oxidative removal of DBT on the selected activated carbons under saturated adsorption. In order to understand the role of activated carbon, a blank test without activated carbon acts as a control experiment. Oxidation products of DBT were analyzed and identified after the reaction, and it was found that DBT was converted to SO_4^{2-} and sulfone.

It can be seen from Fig. 1 that the carbon-formic acid systems have good catalytic activities in the oxidative removal of DBT with hydrogen peroxide, however, the

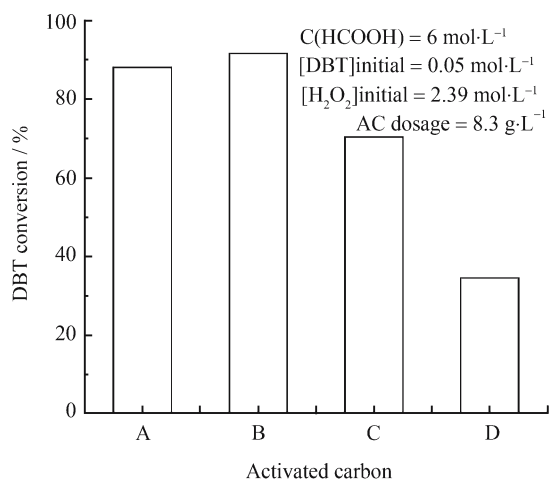


Fig. 1 Conversions of dibenzothiophene in the presence of saturated activated carbons (Reaction temperature 333 K, reaction time 60 min)

A: 602; B: 660; C: ϕ 3.0; D: without activated carbon

catalytic performances of the carbons are different, and that wood carbons such as 660 and 602, have better catalytic performances than coal carbon ϕ 3.0. The control experiment D designated as only formic acid catalysis has low DBT conversion. In the oxidation of DBT with hydrogen peroxide catalyzed by activated carbon-formic acid, formic acid can provide the oxidation reaction system with low pH, which is favorable to the oxidation of DBT on activated carbon, and it interacts with hydrogen peroxide to form performic acid which can oxidize DBT to DBT sulfone. Furthermore, adsorption of DBT on the carbon surfaces and the dispersion of activated carbon in the oil phase or interface phase can increase the collision probability of DBT with the active oxygen species and accelerate the oxidation reaction. Fig. 1 shows that carbon 660-formic acid system has the highest catalytic activity, and DBT conversion reaches 91.6%.

3.2 Effect of activated carbon amount on oxidation of dibenzothiophene

Figure 2 shows that the dynamic reactivity of DBT is a function of the reaction time under different AC amounts, ranging from 2.8 g·L⁻¹ to 19.4 g·L⁻¹. It can be seen that the conversion of DBT increases as the used AC amount increased from 2.8 g·L⁻¹ to 13.9 g·L⁻¹, and DBT dynamic reactivity is highest with 13.9 g·L⁻¹ of AC. For 19.4 g·L⁻¹ of AC used, DBT conversion is highest for the first 10 min, and then levels off after 10 min. DBT conversion versus AC amount increases in this order: 2.8 g·L⁻¹ < 19.4 g·L⁻¹ < 8.3 g·L⁻¹ < 13.9 g·L⁻¹ when the reaction time is 60 min. So, AC amount in the reaction system has an important impact on the oxidation of DBT. Activated carbon in the reaction system has two positive roles: first, it can catalyze hydrogen peroxide to decompose to the active oxygen species (OH· and HO₂·), which can oxidize DBT adsorbed on the AC surfaces; second, activated carbon dispersed in the oil phase can increase the

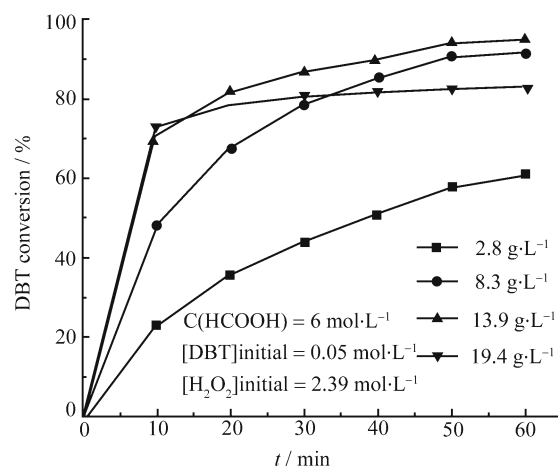


Fig. 2 Effect of 660 dosage on oxidation of DBT (Reaction temperature 333 K, reaction time 60 min)

collision probability of DBT with the active oxygen species, which can accelerate the oxidation reaction. The AC amount used has an impact on the rate of the H₂O₂ decomposition into hydroxyl radicals. The H₂O₂ decomposition rate increases as the AC amount increases when the H₂O₂ concentration and the aqueous pH remain unchanged in the reaction system [13], and then the active oxygen species increase, so the oxidation of DBT is enhanced. However, the H₂O₂ decomposition rate increases as the AC amount continuously increases, so the concentration of active oxygen species rapidly increases in the system, and the decomposition rate of hydroxyl radicals into oxygen increases too [14]. Thus, the AC amount must be optimized to control the production rate and the amount of free radicals so as to improve the availability of H₂O₂.

3.3 Effect of formic acid concentration on oxidation of dibenzothiophene

The oxidation of DBT was carried out with hydrogen peroxide catalyzed by 660 under various formic acid concentrations. Meanwhile, in order to understand the difference between the carbon-formic acid catalytic system and the only formic acid catalytic system, the oxidation of DBT in the presence of only formic acid was carried out as a control experiment. As shown in Fig. 3, 660 has a high catalytic activity when formic acid concentration is zero, and DBT was converted to SO₄²⁻ on activated carbon due to surface hydroxyl radicals. This was confirmed with the addition of BaCl₂ into the resulting aqueous phase, which made a white precipitate with the SO₄²⁻ ion. However, DBT is oxidized to SO₄²⁻ and DBT sulfone in the AC-HCOOH-H₂O₂ system, which are derived from the combination of the hydroxyl radicals and the performic acid generated in the reaction medium. The conversion of DBT increases as formic acid concentration increases in the presence of 660. Meanwhile, the concentration of performic acid in the aqueous phase increases and the aqueous pH decreases, which is helpful in

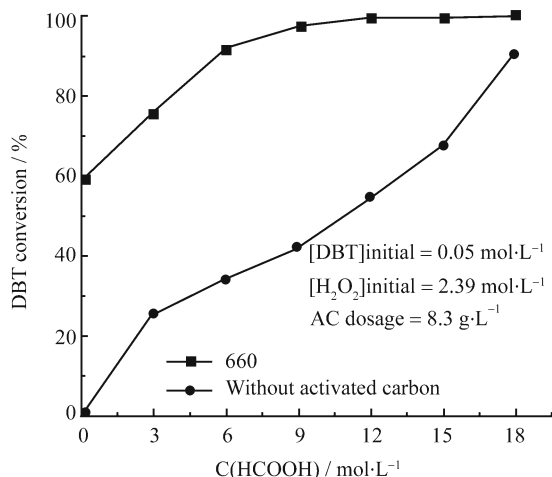


Fig. 3 Effect of formic acid concentration on reactivity of DBT (Reaction temperature 333 K, reaction time 60 min)

catalyzing hydrogen peroxide to produce the active oxygen species. The oxidative removal of DBT is 100% in the presence of 660 when formic acid concentration is 12 mol·L⁻¹.

The increase of DBT conversion with the increase of formic acid concentration in the absence of AC is much lower than that catalyzed by activated carbon-formic acid. In the presence of AC, DBT has high reactivity even for low formic acid concentration. In the HCOOH-H₂O₂ desulfurization system, the fast oxidation rate of DBT must require high HCOOH concentration, which will bring about safety problems in its industrial application. However, in the AC-HCOOH-H₂O₂ system, high HCOOH concentration is not essential for high oxidative desulfurization, so it is safer for industrial application.

3.4 Effect of initial H₂O₂ concentration on dibenzothiophene oxidation

In the AC-HCOOH-H₂O₂ system, H₂O₂ acts as oxidant, and its concentration will influence the production of hydroxyl radicals and performic acid as well as the availability of H₂O₂. In order to investigate the effect of initial H₂O₂ concentration on the oxidation activity of DBT, the oxidation of DBT was carried out under various initial H₂O₂ concentrations at 60°C for 60 min. The initial H₂O₂ concentration was defined as the initial molar concentration of H₂O₂ in the aqueous phase. As shown in Fig. 4, DBT conversion rapidly increased as initial H₂O₂ concentration increased from 1.195 mol·L⁻¹ to 3.187 mol·L⁻¹; but it slowly increased as initial H₂O₂ concentration increased from 3.187 mol·L⁻¹ to 3.983 mol·L⁻¹, and then leveled off when the concentration increased from 3.983 mol·L⁻¹ to 4.78 mol·L⁻¹. When initial H₂O₂ concentration is low in the system, the produced hydroxyl radicals and performic acid will increase as it increases, which will lead to the enhancement of oxidative desulfurization. However, when initial H₂O₂ concentration is too high, it cannot lead to the increase of the decomposition rate of active oxygen species

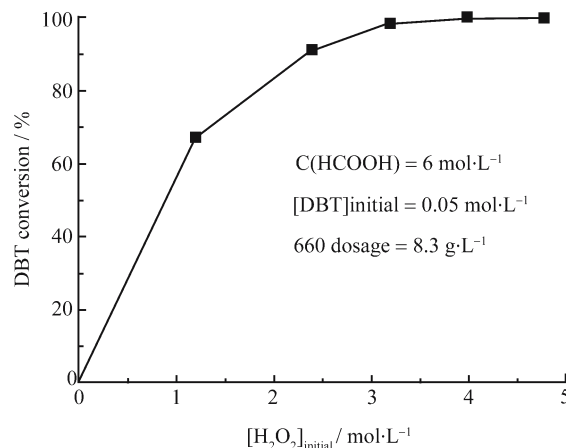


Fig. 4 Effect of initial concentration of H₂O₂ on oxidation of DBT (Reaction temperature 333 K, reaction time 60 min)

into oxygen, so the availability of H₂O₂ will fall off. For the experimental system, it is suitable that initial H₂O₂ concentration is from 2.39 mol·L⁻¹ to 3.187 mol·L⁻¹.

3.5 Effect of initial dibenzothiophene concentration on its oxidative removal

Sulfur content of diesel fuel will influence oxidative desulfurization deepness, oxidant dosage and availability and the desulfurization cost. In order to investigate the effect of initial DBT concentration on its conversion and residual concentration, the oxidative reaction of DBT was carried out under various initial DBT concentrations at 60°C for 60 min with an O/S molar ratio of 12. As shown in Fig. 5, for the same O/S molar ratio and catalyst amount, the higher the initial DBT concentration, the higher the residual DBT concentration is, and the more difficult the deep desulfurization. This suggests that deep desulfurization of diesel fuel with high sulfur content is more difficult than that with low sulfur content, and that the oxidant dosage and desulfurization cost are higher.

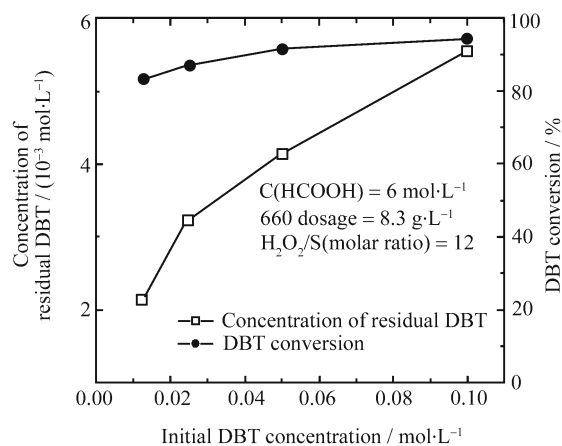


Fig. 5 Effect of initial DBT concentration on oxidative desulfurization (Reaction temperature 333 K, reaction time 60 min)

3.6 Reaction temperature effect

Within the experimental temperature range, the conversion of DBT increases as the reaction temperature increases, as shown in Fig. 6. The production rate of active oxygen species and the oxidation of DBT are promoted as the reaction temperature increases. Therefore, it is advantageous to take a suitable high reaction temperature. For the first 30 min, DBT conversion increases as the reaction goes on, but the reaction rate is quite different at different reaction temperatures for the reaction time from 30 min to 60 min. DBT conversion is constant for the reaction time from 30 min to 60 min at 80°C. Oxidative desulfurization reaches 100% after 30-min reaction.

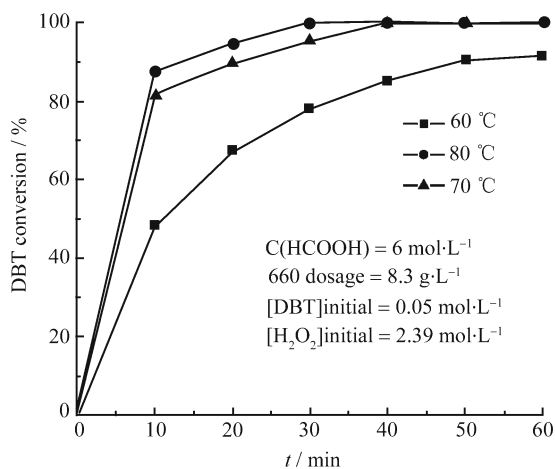


Fig. 6 Effect of reaction temperature on oxidation of DBT

4 Conclusions

(1) In the oxidation of DBT with H_2O_2 , the AC-HCOOH catalytic system is obviously better than only HCOOH catalysis under low HCOOH concentration. This is because H_2O_2 can produce hydroxyl radicals and the performic acid catalyzed by AC-HCOOH, and the addition of AC can increase the collision probability between the reactants. 660 has the highest catalytic activity among the used activated carbons.

(2) For the H_2O_2 -HCOOH-AC system, AC dosage influences the formation rate of active oxygen species (OH^\cdot and HO_2^\cdot) and the reaction contact area, and the formation rate and amount of the radicals were adjusted to enhance the availability of H_2O_2 by controlling AC dosage. Activated carbon has the best catalytic performance when HCOOH concentration in the aqueous phase is $12 \text{ mol} \cdot \text{L}^{-1}$. For the experimental system, it is suitable that initial H_2O_2 concentration is from $2.39 \text{ mol} \cdot \text{L}^{-1}$ to $3.187 \text{ mol} \cdot \text{L}^{-1}$.

(3) For the same O/S molar ratio and catalyst amount, the higher the initial DBT concentration, the higher the residual DBT concentration is, and the more difficult the deep desulfurization. This indicates that oxidative desulfurization technology is suitable in the deep desulfurization of diesel fuel with low sulfur content. It is helpful to take high temperature in oxidative desulfurization. For the oxidative desulfurization of *n*-octane solution with DBT, sulfur removal can reach 100% at 80°C for 30 min.

The results show that H_2O_2 -HCOOH-AC can be applied in deep desulfurization of diesel fuel to produce ultra-low sulfur diesel fuel so as to meet the increasingly severe sulfur content regulation.

References

- Zannikos F, Lois E, Stournas S. Desulfurization of petroleum fractions by oxidation and solvent extraction. *Fuel Process Technol*, 1995, 42: 35–45
- Otsuki S, Nonaka T, Takashima N. Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy & Fuels*, 2000, 14: 1234–1239
- Liu W Y, Lei Z L, Wang J K. Kinetics and mechanism of plasma oxidative desulfurization in liquid phase. *Energy & Fuels*, 2001, 15: 38–43
- Zhao D, Zhang S, Liu C, Wang L. Study on N_2O decomposition over metal oxide catalyst supported by active carbon fiber. *J Chem Eng of Chin Univ*, 2003, 17(3): 289–293 (in Chinese)
- Rodriguez-Reinoso F. The role of carbon materials in heterogeneous catalysis. *Carbon*, 1998, 36: 159–175
- Lu H, Li C. Investigation of adsorption performance of N_2 and O_2 on a carbon molecular sieve. *J Chem Eng of Chin Univ*, 2000, 14(2): 170 (in Chinese)
- Jin Y, Xu H, Xie Y. Adsorption of benzene and toluene vapour on activated carbon. *J Chem Eng of Chin Univ*, 2004, 18(2): 258–263 (in Chinese)
- Hüseyin K, Kadim C. Chemical cleaning of turkish lignites by leaching with aqueous hydrogen peroxide. *Fuel Process Technol*, 1997, 50(1): 19–33
- Takayuki H, Yasuhiro S, Ken O. Effect of photosensitizer and hydrogen peroxide on desulfurization of light oil by photochemical reaction and liquid-liquid extraction. *Ind Eng Chem Res*, 1997, 36(3): 530–533
- Boehm H P. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon*, 1994, 32: 759–769
- Donnet J B. The chemical reactivity of carbon. *Carbon*, 1968, 6: 161–176
- Firth J B, Watson F S. CXCVI-The behavior of activated sugar carbon in contact with hydrogen peroxide solution. *J Chem Soc*, 1923, 123: 1750–1755
- Elmer C L, James H W. Activated carbon as catalyst in certain oxidation-reduction. *J Phys Chem*, 1940, 44: 70–85
- Yoon J, Lee Y, Kim S. Investigation of the reaction pathway of OH^\cdot radicals produced by Fenton oxidation in the conditions of wastewater treatment. *Water Sci Technol*, 2001, 44: 15–21