Removal of Dibenzothiophene in Diesel Oil by Oxidation over a Promoted Activated Carbon Catalyst[1]

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Abstract—Oxidative removal of dibenzothiophene (DBT) in n-octane solution by H_2O_2 on a promoted activated carbon (AC) catalyst was studied. DBT adsorption and catalytic behaviors on AC were examined. Effects of pH in aqueous phase, amounts of AC and formic acid (HCOOH) for promotion as well as initial molar H_2O_2/S ratio were investigated. Experimental results led to conclusion that DBT was readily oxidized by H_2O_2 over an AC catalyst promoted by HCOOH. Suitable amount of AC can improve the activity of H_2O_2 resulting in a deeper extent of sulfur removal. A 100% conversion of DBT in an octane solution by H_2O_2 oxidation was attained on the HCOOH−H_2O_2/AC catalyst at 80°C for a reaction time of 30 min.

INTRODUCTION

Because of increase in the environmental concern, concentration of sulfur in fuels is limited severely and its regulation level is becoming lower and lower from year to year. Under these situations, many researchers have been developing highly active catalysts for ultra deep hydrodesulfurization (HDS) of diesel fuels to meet these sulfur regulations [1]. However, it needs more severe reaction conditions, resulting in large hydrogen consumption and a reduction of catalyst life that lead to increasing operating expenses [1]. This fact has stimulated the search for alternative new technologies for deep or total desulfurization of diesel fuel products. Compared to traditional HDS processes, oxidative desulfurizaiton (ODS) has several advantages, including mild reaction conditions (atmospheric pressure and relatively low temperatures), no hydrogenation environment and the feasibility to remove sterically hindered sulfides [2, 3]. Therefore, studies on ODS process using different oxidizing agents such as NO_2 [4], *tert*-butyl-hydroperoxide [5, 6] and H_2O_2 have been reported in the literature. H_2O_2 is the most common oxidant agent, because it is environmentally friendly. Therefore, H_2O_2 was often used in the presence of a catalyst composition in this decade to produce oxygen-containing chemicals, such as acetic acid [7, 8], formic acid [9, 10], polyoxometalate [11, 12], CF_3COOH [13], titano silicates [14], solid bases [15], sodium tungstate-acetic acid [16], ionic liquids [17], and Mo/Al_2O_3 [18].

In addition, activated carbon (AC) is widely used as an adsorbent of organic contaminants due to its porous and large specific surface area characteristics. Nowadays, activated carbon has been involved in an increasing number of catalytic reactions. It was applied either as a support for the active phases or as a main catalyst component owing to its physical performance and oxygen-containing surface functional groups [19]. As a good example, catalytic wet oxidation is a well-developed method to remove hazardous substances by using these active oxidation catalysts under relatively mild conditions [20−23]. The hydroxyl radicals produced during the activation of hydrogen peroxide by activated carbon is such a strong oxidizing agent that is able to oxidize organic compounds under ambient conditions [24]. The hydroxyl radicals produced from hydrogen peroxide can be resonance-stabilized on the carbon surfaces [25, 26], which results in the oxidation of heterocyclic organic sulfur compounds to form SO_4^{2-} [27, 28]. AC has a strong affinity for oil phase that would wet it through to interact with hydrogen peroxide in aqueous phase. It was observed that DBT was dramatically oxidized by H_2O_2 over this HCOOH promoted AC catalyst by the combination of hydroxyl radicals and performic acid formed in the reaction system. Our work was focused on studying contaminant DBT adsorption and des-

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Structural parameters calculated from sorption of nitrogen at 77 K and DBT adsorption capacity of the AC

Sample	S_{BET}, m²/g	V_{total}, cm³/g	V_{micr}, cm³/g	Mesopore volume, %	Adsorption capacity, g of DBT/g of adsorbent
W660	2115	1.284	0.244	81.0	0.125
W602	2007	1.177	0.284	75.9	0.124
W269	1858	1.084	0.318	70.7	0.123
C30	1496	0.738	0.440	40.4	0.107
C15	1574	0.651	0.579	11.1	0.105
C830	1247	0.814	0.358	56.0	0.112

ulfurization on AC surface in a single reactor directly producing lower residual sulfur content of diesel oil products without succeeding separation processes, and on a comparison with other catalytic ODS unit in the published papers. Additionally, the oxidation behaviors of DBT by H_2O_2 over AC type catalyst and the promotion effect of formic acid were also elucidated.

EXPERIMENTAL

Materials and Apparatus

H_2O_2 (30% wt) (AR, analytically pure reagent) was obtained from Shanghai Pengpu Chemicals. Dibenzothiophene (DBT) (AR) was obtained from ACROS Organics. Formic acid (AR) and *n*-octane (CP-Chemically pure reagent) were purchased from Shanghai Lingfeng Chemicals. C15, C30, and C830 were granular coal-based, steam-activated carbons (sieved into 40~60 mesh; ferric salt content less than 0.2% wt). W602, W269, and W660 were powder wood-based, phosphoric acid-activated carbons (80~100 mesh). All the activated carbons in this study were obtained from Shanghai Activated Carbon Co. The carbons were treated with concentrated hydrochloric acid and hydrofluoric acids, and then repeatedly washed with deionized water till the filtrate had the same pH value as deionized water. They were then dried in an air oven at 120°C overnight. DBT content was analyzed by using a GC920-FPD gas chromatograph with a capillary column, designated as HP-5 and flame photometric detector (FPD)).

Textural Structure of Activated Carbon

Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at 77 K. Before the experiment, samples were heated at 393 K and then degassed at this temperature for 5 h under 10^{-5} Torr. These isotherms were used to calculate the specific surface area (designated as S_{BET}) by BET method and micropore volume (V_{micr}) by BJH method, whereas the total pore volume (V_{total}) was calculated from the volume of nitrogen adsorbed at $p/p_0 = 0.977$.

Adsorption of DBT

To examine DBT adsorption capacity on the carbons, 72 ml of DBT-containing *n*-octane solution with the initial concentration of 0.556 g/l (based on sulfur content) were taken and put in a flat bottom flask with 1.0 g of activated carbon. The mixture was stirred continuously at 25°C for 12 h and then filtrated. The amount of DBT adsorbed by the activated carbon after 12 h was calculated as follows:

$$Q = [72 \times 10^{-3}([S]_0 - [S]) \times 184]/[32 \times M],$$

where *q* is the amount of DBT adsorbed on the carbons after 12 h (g of DBT/g of carbon); $[S]_0$ is the initial concentration of sulfur in the *n*-octane solution; [S] is the sulfur content in the filtrate; M is the amount of the carbon used; 184 denotes the molecular weight of DBT; and 32 is the atomic

Oxidation of DBT on Promoted AC under Various pH Values

Our experimental procedure was as follows: 36 ml of DBT-containing *n*-octane solution with initial sulfur concentration of 0.556 g/l and activated carbon were added to a 100 ml three-necked flask, fitted with a condenser, a mechanical stirrer and a thermometer. At the same time the required quantity of 30% wt H_2O_2 solution and deionized water were introduced to a 20 ml beaker where pH of the mixture was adjusted by using hydrochloric acid and sodium hydroxide solutions. The H_2O_2 solution (7 ml) was transferred to the reaction flask which has already been heated to 60°C. The reaction mixture was kept at 60°C for 60 min while stirring with 750 rpm and then the oil phase was separated.
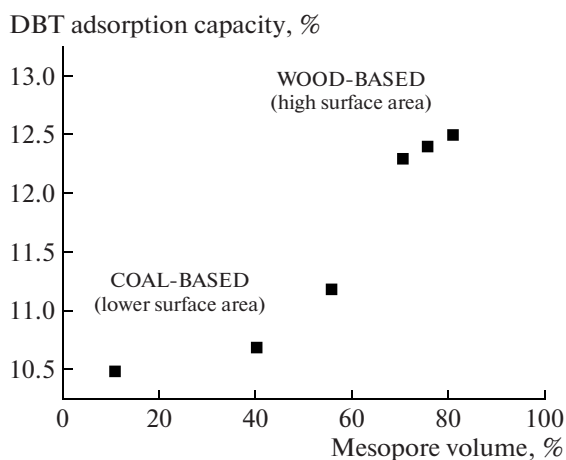
Fig. 1. Variation DBT adsorption capacity with mesopore volume.

Fig. 2. DBT conversion on the saturation adsorbed carbons: (*1*) W660, (*2*) W602, (*3*) W269, (*4*) C830, (*5*) C30, (*6*) C15. Conditions: temperature 333 K; $[S]_0 = 0.556$ g/l; $[H_2O_2]_0 = 12.5$ mmol; pH 2.0(HCl); AC, 0.3 g.

RESULTS AND DISCUSSION

Relationship between Tissue Structure of AC and its DBT Adsorption

The structural characteristics of AC from different sources derived from nitrogen adsorption isotherms at 77 K are summarized in table. The mesopore volume percentage of the carbons decreases in the order: W660 > W602 > W269 > C830 > C30 > C15. Thus, a wood-based carbon (designated as W660) exhibits the largest surface area and mesopore volume percentage.

In order to elucidate the role of DBT adsorption on AC in the oxidation reaction, the adsorption behaviors of DBT in *n*-octane solution on AC are first examined (table). A close relationship between percent of DBT adsorption capacity and percent of mesopore volume is also illustrated by Fig. 1. It is clear that adsorption capacity of AC made from wood is higher than that from coal due to the larger surface area and mesopore volume percentage. The larger mesopore volume percentage and surface area of the AC, the higher its DBT adsorption capacity (Fig. 1). These results reveal that DBT adsorption capacity is predominantly determined by

Oxidation of DBT by H_2O_2 over AC Type Catalysts

In our tests, the AC were first thoroughly saturated with DBT by impregnation with DBT-containing *n*-octane solution for 12 h to avoid removal DBT in the reaction system. Figure 2 shows the DBT oxidation behaviors on AC saturated by DBT. It is seen that the AC must have good catalytic activities for the oxidation of DBT with hydrogen peroxide. Activated carbon would catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals as a strong oxidizing agent [29]. Surface reactions on the carbon surfaces resulting from thermal influences often obey free
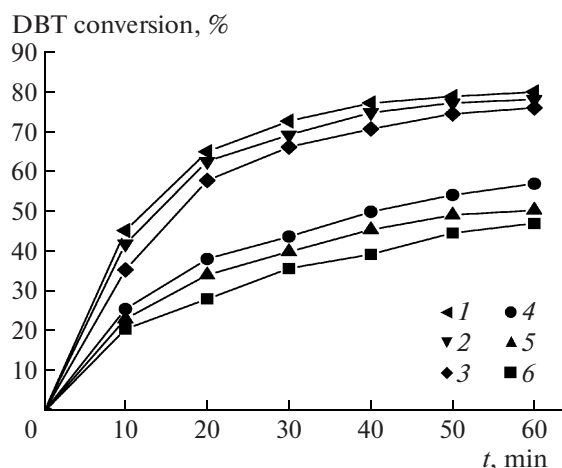
radical mechanisms. These reactions involve neither ions nor free electrons but attached atoms [30]. This indicates that electron transfer reactions would easily take place on carbon surfaces. The radicals produced during the surface reactions are likely to be resonance-stabilized on the carbon surfaces [25, 26]. So the radicals have enough time to oxidize the sulfur compound on the carbons. The sulfur compound was suggested to be finally converted to SO_4^{2-} and thus removed into the aqueous phase as well. This was proved by addition of $BaCl_2$ into the resulting aqueous phase, resulting in a white precipitate with SO_4^{2-} ions.

However, catalytic activities varied for each kind of AC. The carbons made from wood have better catalytic performances than that from coal base. The catalytic activity of the AC decreased in this order: W660 > W602 > W269 > C830 > C30 > C15. It was seen from results in Fig. 1 and table that the higher, the AC adsorption capacity, the higher the catalytic performance. Comparing the correlation between DBT oxidation and adsorption behaviors on the AC, it was concluded that carbon surface would accelerate the oxidation of DBT and it might hence be more advantageous to the oxidation of DBT on the AC with higher adsorption abilities.

Effect of the Aqueous Phase pH Value on Catalytic Activities of AC

In order to investigate the effect of the aqueous phase pH value on the catalytic activity by H_2O_2 oxidation over promoted AC, the DBT oxidation tests were performed under various pH values that were adjusted by adding hydrochloric acid and sodium hydroxide solutions. Figure 3 showed the DBT oxidation extent as a function of pH value over each hydro-
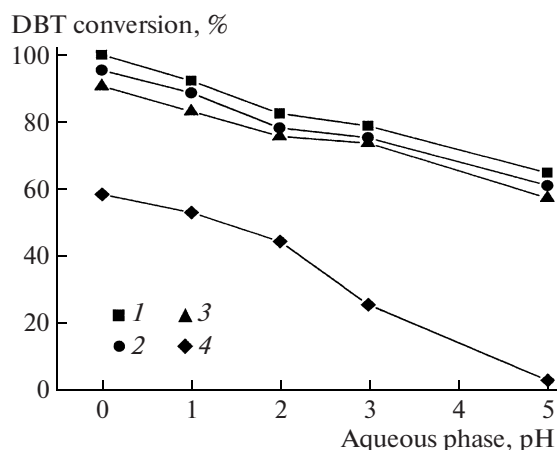
DBT conversion, %
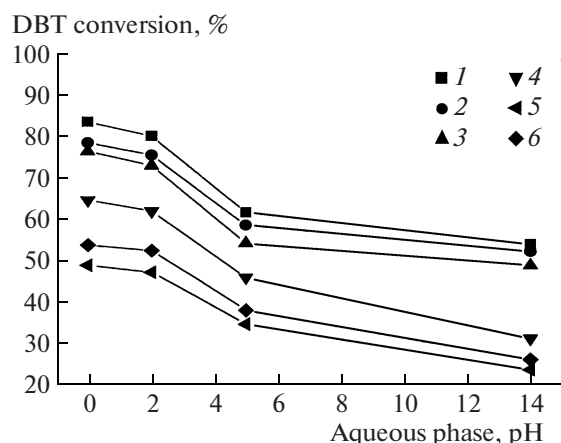
Fig. 3. Effect of pH adjusted by HCl on oxidation of DBT on the selected AC: (*1*) W660, (*2*) W602, (*3*) W269, (*4*) C830, (*5*) C30, (*6*) C15. Conditions: temperature 333 K; reaction time 60 min; $[S]_0 = 0.556$ g/l; $[H_2O_2]_0 = 12.5$ mmol; AC, 0.3 g.

Fig. 4. Oxidation of DBT over HCOOH-HCOOH–H_2O_2/AC: (*1*) W660, (*2*) W602, (*3*) W269, (*4*) without AC. Reaction conditions: temperature 333 K; reaction time 60 min; $[S]_0 = 0.556$ g/l; $[H_2O_2]_0 = 12.5$ mmol; AC dosage, 0.3 g.

gen peroxide/AC. It was clearly observed that the oxidative removal extent of DBT reached a minimum at pH of 14 and increased in decreasing pH value. The decomposition rate of hydrogen peroxide on AC forming hydroxyl radicals was reported to be dependent on the aqueous phase pH and was investigated in the range from 2.6 to 9.5 [31]. From their results, the decomposition rate of hydrogen peroxide increased as the aqueous pH decreased when it was less than 4. On the contrary, it was concluded that the decomposition rate of hydrogen peroxide to produce oxygen rapidly increases in alkaline medium [32]. These results might be explained by the difference in redox potential. In the literature, it was published that, in a pH of 0 aqueous solution, the redox potential is +1.77 V for hydrogen peroxide and +2.8 V for hydroxyl radicals, whereas, in an aqueous solution with a pH of 14, the redox potential is +0.88 V for hydrogen peroxide and +2.0 V for hydroxyl radicals [33]. These data revealed that it is more advantageous to the oxidation reaction in a low pH aqueous phase.

Promotion Effect of Formic Acid

It was reported that DBT might be oxidized to form the corresponding sulfone by 30% wt hydrogen peroxide only in the presence of formic acid or glacial acetic acid [8–10]. From the results discussed in the above section of this work, it was advantageous for the oxidation of DBT on hydrogen peroxide over the carbons at aqueous phase pH value of less than 2. Therefore, it must be necessary to introduce acids to the reaction system for the oxidation of DBT. In this paper, the effect of the introduction of formic acid to the oxidation of DBT over H_2O_2/AC was investigated. In our tests here, AC materials were made mainly from wood

and various pH values were adjusted by the addition of formic acid. For comparison, a DBT oxidation test was also performed only in the presence of formic acid as a catalyst. As shown in Fig. 4, the reactivity of DBT increased as the aqueous pH decreased in the presence of the wood-based carbons. Without AC in the reaction system, the increase in DBT conversion in decreasing aqueous pH was much lower than that with AC. Comparing Figs. 4 and 3, it was observed that the addition of formic acid gave much more dramatic impact on activity than hydrochloric acid. The former acid resulted in ~5% increases in DBT conversion at pH value of 5 or 2 and a ~20% increase at pH 0. In the oxidation of DBT with H_2O_2 over HCOOH promoted AC catalysts, formic acid has two roles: firstly, it provides a low pH circumstance in the reaction system which is favorable to the oxidation of DBT on AC; secondly, it may interact with hydrogen peroxide to form per-formic acid to stimulate DBT oxidation which is also promoted by the increase of formic acid concentration in the aqueous phase. In short, the oxidation activity of DBT over wood-based carbons is promoted by formic acid.

Effect of AC Amount on DBT Conversion

Figure 5 showed some data referring to the influence of AC amounts ranging from 0.1 to 0.7 g on the DBT dynamic reactivity at various reaction times. It was seen that DBT conversion increased as AC amount increased from 0.1 to 0.5 g, reaching a maximum at 0.5 g. When 0.7 g of AC were used, DBT conversion reached up to the highest at 10 min, whilst almost kept unchanged at longer reaction times. For a reaction time of 60 min, DBT conversion referring to the AC amount increased in this order: 0.1 < 0.7 < 0.3 <
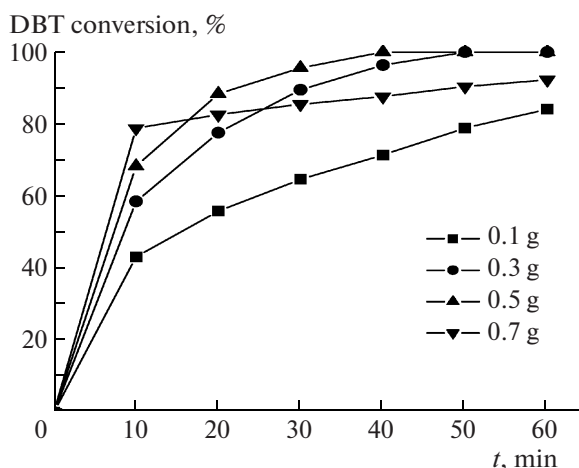
Fig. 5. Effect of W660 amount on oxidation activity of DBT. Reaction conditions: temperature 333 K; $[S]_0 = 0.556$ g/l; pH 0 (HCOOH); $[H_2O_2]_0 = 12.5$ mmol.

0.5 g at 60. Therefore, AC amount in the reaction system must give an important impact on DBT oxidation activity.

Several electron transfer schemes have been proposed as H_2O_2 decomposition mechanisms over ferrous iron (Fe^{2+}) containing catalysts. According to these mechanisms, the reaction should be initiated by a reduction site transferring an electron to H_2O_2 to produce a $HO^{\bullet}$ radical or initiated by a peroxide transferring an electron to an oxidizing site to produce a $HOO^{\bullet}$ species [34−37]. Reducing sites and oxidizing sites on the active carbon in our tests would be similar to the action of Fe^{2+} and Fe^{3+} in the decomposition of H_2O_2 over AC. Therefore, a simple competitive mechanism was proposed in Fig. 6 for the H_2O_2 reactions in the presence of AC. The reactions initiated from the activation of H_2O_2 by a reducing site in a Fenton-like reaction [33, 38−41] to produce a HO radical intermediate. The hydroxyl radical should then react

according to two competitive pathways. Firstly, it reacted with another H_2O_2 molecule resulting in the decomposition to produce O_2. Secondly, it oxidized DBT. From Fig. 6, it was clear that increase in AC amount would accelerate the H_2O_2 decomposition and the increase in H^+ ion concentration by adjusting pH value in the aqueous phase must inhibit the decomposition reaction to O_2. Therefore, the addition of formic acid and the control of the AC amount used must improve the availability factor of H_2O_2.

Initial Molar H_2O_2/S Ratio

In order to investigate the effect of initial molar H_2O_2/S on the reactivity of DBT over W660, the oxidation of DBT was carried out under various initial molar H_2O_2/S at 60°C for 60 min and at 80°C for 30 min respectively. As shown in Fig. 7, reactivity of DBT increased in increasing initial molar H_2O_2/S up to 12 and then remained unchanged at 60°C for
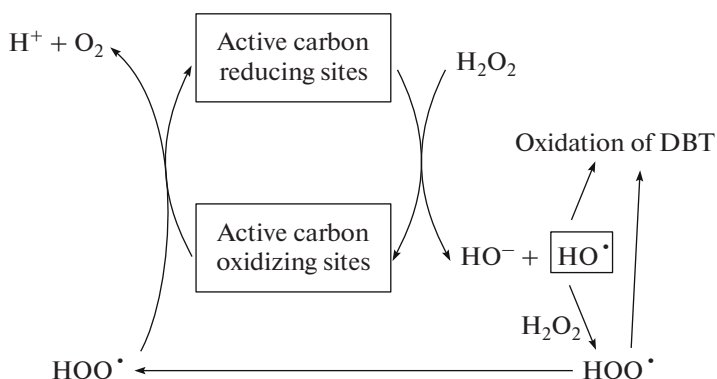

Fig. 6. Proposed competitive mechanism for DBT oxidation over $HCOOH−H_2O_2$/AC.
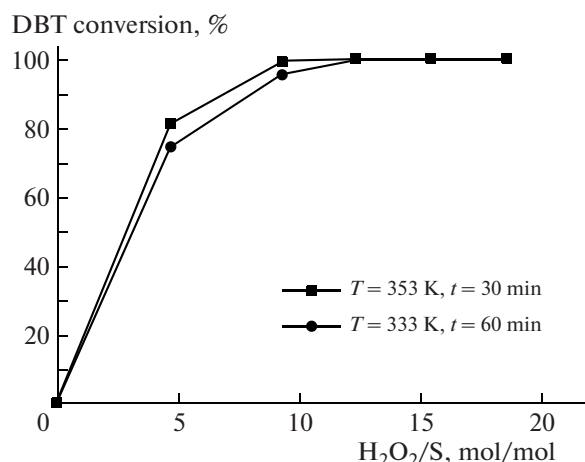
DBT conversion, %

Fig. 7. Effect of initial H_2O_2/S molar ratio DBT conversion. Reaction conditions: W660, 0.5 g; pH 0 (HCOOH); $[S]_0 = 0.556$ g/l.

60 min. If the reaction was performed at 80°C for 30 min, this initial H_2O_2/S molar ratio was 9. For the formic acid-AC catalysts, the initial molar H_2O_2/S determines the initial hydrogen peroxide concentration in the reaction, which has an important impact on the formation of both hydroxyl radicals and performic acid. DBT conversion increased as the initial H_2O_2/S molar ratio is higher due to the formation of more hydroxyl radicals and performic acid. On the other side, Fig. 5 showed that too high initial H_2O_2/S molar ratio resulted in the decomposition of H_2O_2 into oxygen, which led to loss of H_2O_2. So the initial H_2O_2/S molar ratio should be well controlled. From Fig. 7, DBT conversion at 80°C for 30 min reached 100% which was higher than that performed at 60°C for 60 min. Moreover, the higher reaction temperature (80°C) would save the expense for hydrogen peroxide because of lower initial H_2O_2/S molar ratio. The formation of active oxygen species may accelerate the oxidation reaction, when the reaction temperature increased from 60 to 80°C.

CONCLUSIONS

Oxidation of DBT in *n*-octane solution by hydrogen peroxide over formic acid promoted activated carbon catalysts was studied. Adsorption capacity of the wood-based carbons for DBT is higher than that of the coal-based carbons owing to their different pore structures. It was concluded in this work that the higher the DBT adsorption capacity on the activated carbons, the higher the catalytic performance for DBT oxidation. In addition, the conversion must be enhanced at lower aqueous phase pH value. The introduction of formic acid accelerated DBT oxidation over AC. For wood-base W660, DBT conversion as a function of AC amount increased in the order of: 0.1 < 0.7 < 0.3 <

0.5 g. In addition, AC amount should be well controlled to improve the availability factor of H_2O_2. Proposed competitive mechanism for DBT oxidation with H_2O_2 over HCOOH−AC catalysts elucidated the function of formic acid addition and satisfactory control of the used AC amount would improve the availability factor of H_2O_2. Initial molar ratio H_2O_2/S should also be controlled in this reaction system. The formation of the active oxygen species may increase and accelerate the reaction rates when the reaction temperature raised from 60 to 80°C. Treatment of DBT in octane solvent with H_2O_2 over HCOOH-AC catalyst system performs 100% conversion at 80°C for 30 min.

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