Chemical Engineering Journal 156 (2010) 528–531

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Photocatalytic oxidation dibenzothiophene using TS-1

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ARTICLE INFO

Article history:
Received 17 October 2008
Received in revised form 18 March 2009
Accepted 2 April 2009

Keywords:
Dibenzothiophene
Photocatalytic oxidation
TS-1

ABSTRACT

Photocatalytic oxidation of dibenzothiophene (DBT) with hydrogen peroxide using TS-1 as photocatalyst at ultraviolet lamp irradiation has been studied. The result showed DBT was photooxidized successfully, regardless of steric limitations. Optimal reaction conditions were investigated in detail. Photooxidized products of DBT are DBT 5-oxide, DBT 5,5-dioxide and SO_4^{2-} by mass spectrum. Kinetics parameters of the photocatalytic oxidation of DBT were measured and calculated. The kinetics of photocatalytic oxidation of DBT is fist-order. Mechanism of photocatalytic oxidation of DBT by TS-1 was analyzed.

1. Introduction

In order to protect against environmental contamination, the sulfur level in diesel fuels is presently limited to 15 ppm in Japan, Europe and US [1]. The presence of sulfur in fuels is considered a major source of atmospheric pollution because sulfur atmospheric discharge from combustion is a precursor of acid rain due to the formation of sulfur oxides. A new approach is needed which is not limited to the conventional hydrodesulfurization (HDS) method for the development of an energy-saving desulfurization process. Some oxidative desulfurization processes which include oxidation of dibenzothiophene (DBTs) with oxidants followed by the removal of products have been investigated [2–5]. Oxidative desulfurization (ODS) is considered to be one of the promising new methods for deep desulfurization of fuel oil. Compared with conventional HDS, ODS can be carried out under very mild conditions: at room temperature and under atmospheric pressure. Due to increasing demand for clean and environmentally benign technologies in chemical process engineering, much attention has recently been paid to the establishment of ecologically more acceptable catalytic processes. Titanium silicalite zeolite is a novel catalyst, which is able to catalyze a series of selective oxidations such as aromatic hydroxylations, alkane oxidations, and alkene epoxidations. Recently, several studies have been performed for the catalytic oxidation of organic sulfur compounds over Ti-containing zeolite under mild conditions [6–8]. No result has been reported about effective photocatalytic oxidation using Ti-containing zeolite in desulfurization of fuel oil.

The utilization of the zeolite cavity and framework is attractive to the design and application of highly efficient and selective photocatalytic systems, because zeolites provide unique micropore reaction fields, an unusual internal surface topology, and an ion exchange capacity as well as molecular condensation effect [9]. Recently, zeolites involving transition metal ions within the zeolite framework have opened new possibilities in many research areas not only for catalysis but also for various photochemical processes. K. Lingyan et al. [10] found small molecule thiophene was oxidized completely by TS-1 and hydrogen peroxide (H_2O_2), while DBT could not been oxidized due to steric limitations. In Ti-containing zeolite, –Ti–O–Ti–O– quantum semiconductor nanowire chains show photocatalytic activity for the oxidation of organic compounds [11,12]. In this study, we try to study whether DBT was oxidized with TS-1 at ultraviolet light irradiation.

2. Experimental

2.1. Photocatalytic experiments

Photooxidation experiments were carried out as follows: an *n*-octane (Alfa Aesar company) solution of DBT (Alfa Aesar company) (10 mL, sulfur content 1000 μg/g), 10 mL H_2O_2 and H_2O [H_2O_2 (30%):H_2O = 3:7 volume ratio] were placed in a quartz tube and 0.1 g amount TS-1 (Changling catalyst company of China) was added to the solution. Prior to illumination, the reaction suspension was stirred continuously in the dark for 1 h to ensure adsorption/desorption equilibrium.

The solution was photoirradiated for 2.5 h with magnetic stirring. Reactant samples were collected and analyzed to determine substrate concentration and reaction products at intervals of 30 min

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doi:10.1016/j.cej.2009.04.032

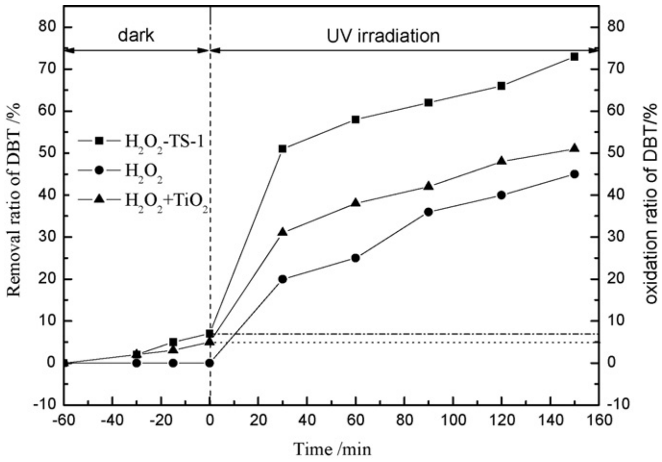


Fig. 1. Removal ratio of DBT under different conditions.

by gas phase chromatogram (GC-7890II, ShangHai) and mass spectrometer (MS-2010EV, Shimazu, Japan).

3. Results and discussion

3.1. Comparison of photocatalytic performance with TS-1 and TiO_2 in the presence of H_2O_2

The effect of TS-1and TiO_2 on the removal ratio of DBT in *n*-octane by UV lamp irradiating was shown in Fig. 1. In the absence of catalyst or UV irradiation, almost no oxidization of DBT was observed. However, the addition of photocatalyst TiO_2 promotes the oxidations of DBT, since the rate of $^{\bullet}$OH formation and charge transfer can be accelerated by the addition of photocatalyst. The removal ratio of DBT decreased dramatically after the addition of TS-1 in the solution. TS-1 exhibits better catalytic performance than TiO_2 in oxidizing DBT, because TiO_2 in the water will form emulsion, which cannot contact fully with oil layer, and can not absorb UV light well. The TS-1 consists of the highly dispersed isolated tetrahedral titanium oxide species in their framework [9]. The lifetimes of the charge transfer excited state of the TS-1 were determined to be much longer than that of the TiO_2 powder. Such a long lifetime of the charge transfer excited state is well associated with the presence of highly dispersed tetrahedral titanium oxide species in TS-1. It seems that photocatalytic oxidation of DBT occurred on the surface of TS-1, because DBT cannot enter into inside of TS-1 which is a kind of micropore zeolite.

3.2. Optimization of reaction condition

In order to screen optimal reaction condition, amount of TS-1 and concentration of H_2O_2 were investigated in detail. In this experiment, one of conditions was changed, while other conditions were immovable, irradiation time is 2.5 h. Two major reaction conditions were selected to investigate. The results were shown in Table 1. An increase of removal ratio of DBT occurred as photocatalyst amount and H_2O_2 concentration was increased. However, with the more photocatalyst and H_2O_2 added into the reaction mixture, the removal ratio of DBT did not increase obviously, even decreased a little. The reason is that photocatalyst is one of the important roles in photocatalysis reaction, increasing photocatalyst amount accelerated charge transfer and generation of hydroxyl free radical ($^{\bullet}$OH), consequently accelerated photocatalytic oxidation of DBT. However, excessive photocatalysts would shield part UV light source, which influences reaction rate, in addition, too much photocatalysts would be wasted. H_2O_2 is the source of hydroxyl free radical ($^{\bullet}$OH), which has strong oxidizing property; increasing H_2O_2 concentration accelerated generation of hydroxyl free radical ($^{\bullet}$OH), consequently accelerated photocatalytic oxidation of DBT, while excessive amount of H_2O_2 would poison surface Ti [7]; and also, too much H_2O_2 would consume some hydroxyl free radical ($^{\bullet}$OH). So, optimization of reaction condition is that amount of TS-1 is 0.1 g/10 mL model diesel and H_2O_2 (30%) concentration is 9% (volume percent, 3 mL).

Table 1
Removal ratio of DBT in different reaction condition. (A) the amount of photocatalyst; (B) H_2O_2 concentration.

Reaction condition	A (g)	B (mL)	Removal ratio of DBT (%)
A	0.05	3	50
A	0.08	3	60
A	0.1	3	73
A	0.12	3	72
A	0.15	3	70
B	0.1	1	65
B	0.1	2	70
B	0.1	5	60
B	0.1	8	50

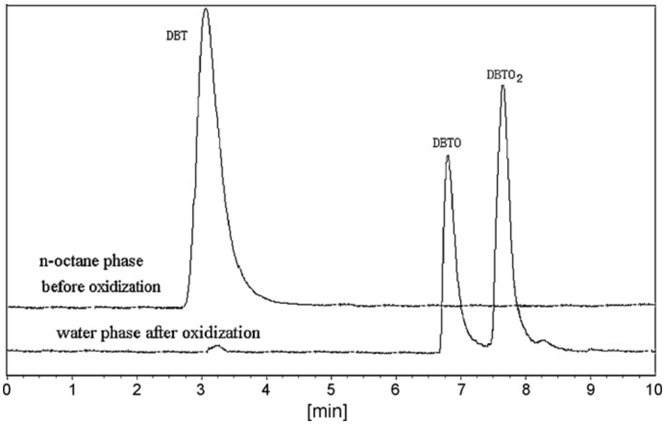


Fig. 2. Gas chromatogram of oxidized and unoxidized DBT.

3.3. Products formed by photocatalytic oxidation of DBT

We did not detect other oxidized products by gas phase chromatogram (GC-7890II, ShangHai) in oil layer, while detected two products in water phase (Fig. 2). We detected fragmentation peaks at *m*/*z* 200 of DBT 5-oxide and those at *m*/*z* 216, 187 of DBT 5,5-dioxide by mass spectrum (Cation, MS-2010EV, Shimazu, Japan) in water phase (Fig. 3). So, we confirm that photocatalytic oxidized products of DBT are DBT 5-oxide, DBT 5,5-dioxide. It shows oxidized products of DBT transfer to water phase fleetly for their higher polar property. In addition, when $Ba(NO_3)_2$ solution was dropped into water phase, white deposit appeared. This suggests that $SO_4{}^{2-}$ is also one of photocatalytic oxidized products of DBT.

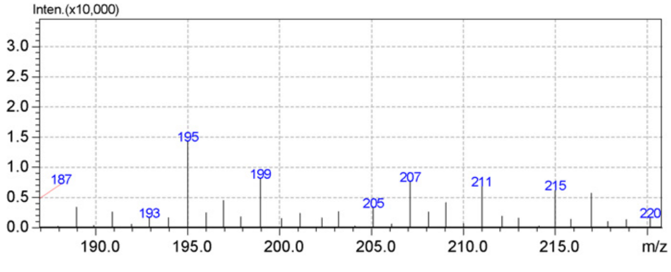


Fig. 3. Mass spectrogram oxidized products of DBT.

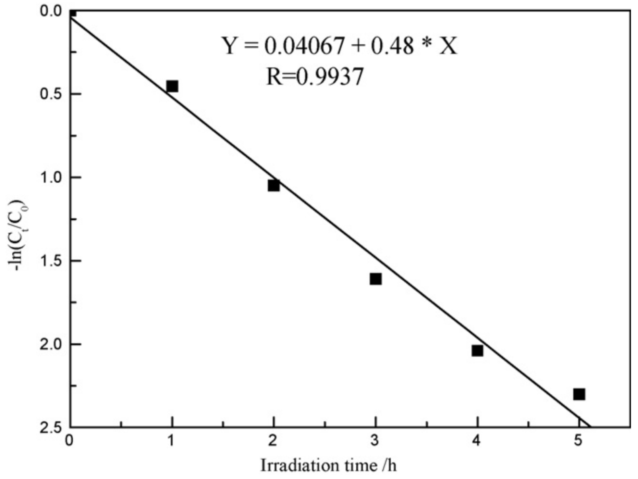
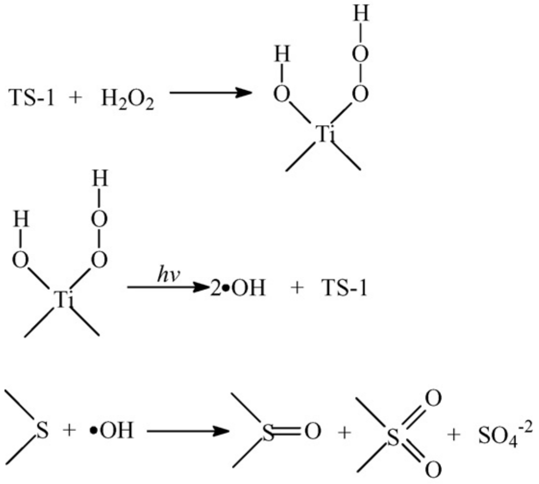


Fig. 4. Pseudo-first-order kinetics for photooxidation of DBT.



Scheme 1. Mechanism for photocatalytic oxidation of DBT.

3.4. Kinetics of photocatalytic oxidation of DBT

Reaction kinetics is of great importance in explaining the reaction mechanism. Experiments to obtain kinetics parameters of the oxidation of DBT were carried out under optimal reaction condition.

The rate constant for the apparent consumption of DBT was obtained from the pseudo first-order equation:

$$-\ln\frac{C_t}{C_0} = k_p t \qquad (1)$$

where C_0 and C_t are the concentrations of substrate at time zero and time t (s), and k_p the first-order rate constant (s^{-1}).

When $-\ln(C_t/C_0)$ was plotted against t, a straight line was fitted to the data (Fig. 4), and the obtained correlation factor ($R = 0.9937$) suggested that DBT photooxidation reaction by TS-1, H_2O_2 and UV light irradiation follows first-order kinetics.

3.5. Mechanism analysis of photocatalytic oxidation of DBT

Ravinder et al. [13] present that oxidation route of small molecule thioether is following as Fig. 5. The ability of titanium silicate molecular sieves to bind H_2O_2 is attributed to the formation of peroxo-species **4** as shown in Scheme 1. The Ti-silicate framework is believed to have species **1** or **2,** which on reacting with H_2O_2 led first to species **3,** similar to Caro's acid, and then to species **4,** providing the reactive O* species required for oxidation.

However, mechanism of photocatalytic oxidation of DBT using TS-1 and H_2O_2 at UV irradiation is different. It has been reported that electron transfer can occur between the –O–Ti^{4+}–O– semiconductor chains and guest species in the pores for some Ti-containing zeolites [14]. It has been reported that Ti-containing zeolites could be used as single-site photocatalyst [15] and Ti atoms in the framework of zeolites could act as photocatalytic active sites. The –O–Ti^{4+}–O– chain could accept the injected electrons from the excited dye and form the species similar to the charge-transfer excited state, which is usually produced over single-site photocatalysts under irradiation [16]. Fig. 6 is the UV–vis spectrum of TS-1. There is an intense adsorption signal at 230 nm, which is characteristic of tetrahedrally coordinated Ti^{4+} ions [17]. Considering that anatase displays a characteristic bandcentred at 330 nm [18], it would be useful to determine if this species is or not present in order to carry out a more accurate assignment of the titanium species present. It also shows there are not extra-framework titanium species in the sample.

On the other hand, it was reported that unstable hydroperoxidic species are easily formed by the interaction of framework titanium in TS-1 with H_2O_2 [13,19]. In this work, white TS-1 powder became light yellow when TS-1 was immersed in aqueous solution of H_2O_2, indicating the formation of titanium-hydroperoxide

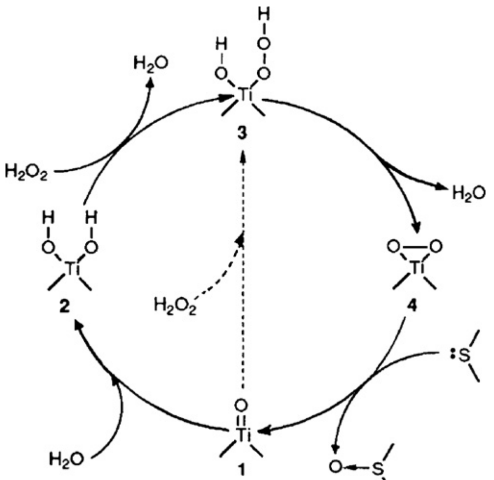


Fig. 5. Oxidation route of thioether using TS-1 and H_2O_2.

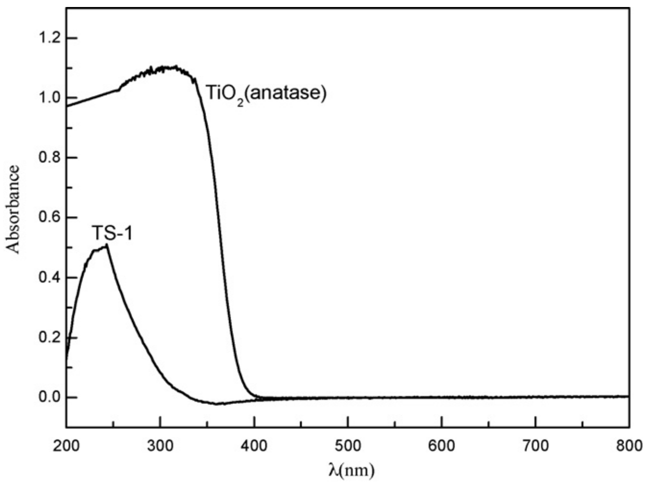


Fig. 6. The UV–vis spectrum of TS-1 and TiO_2.

by the direct interaction of TS-1 with H_2O_2 [20]. Karlsen et al. [21] reported that the O–O bond length in the titanium-hydroperoxide species formed by the interaction of TS-1 with H_2O_2 is 1.52 Å; this represents a remarkable activation of the O–O bond in the titanium-hydroperoxide species compared to that in H_2O_2. Therefore, it could be deduced that, under UV illumination, $^{\bullet}OH$ radical can be formed more easily from titanium-hydroperoxide species than H_2O_2 can be formed [22]. On the basis of the above factors, the possible mechanism for photocatalytic oxidation of DBT is as follows:

4. Conclusion

The mentioned results show DBT can be oxidized successfully using TS-1 as photocatalyst at UV light irradiation, regardless of steric limitations. Photooxidized products of DBT are DBT 5-oxide, DBT 5,5-dioxide and SO_4^{2-} by mass spectrum. The kinetics of photocatalytic oxidation of DBT is fist-order. Mechanism analysis suggests DBT oxidization reaction is due to Ti active species on the surface of TS-1 by UV light irradiating. Further study for improvement of catalytic activity by enlarging pore of TS-1 using acid or altering TS-1 with mesopore Ti-containing zeolite is now underway.

Acknowledgements

This research was supported by grant 20276015 from the National Natural Science Foundation of China and grant 203364 from the National Natural Science Foundation of HeBei province.

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