

Titanium Dioxide Catalyzed Visible-Light-Induced Oxidation of Dibenzothiophene and Application to Desulfurization from Liquid Fuels

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<https://hdl.handle.net/2324/7443249>

出版情報 : Kyushu University, 2025, 博士 (理学), 課程博士
バージョン :
権利関係 :



**Titanium Dioxide Catalyzed
Visible-Light-Induced
Oxidation of Dibenzothiophene and
Application to
Desulfurization from Liquid Fuels**

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February 2026

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Abstract

To reduce the environmental impact of fossil fuel utilization, desulfurization processes are essential. However, even with current hydrogenation desulfurization methods, thoroughly removing difficult-to-desulfurize sulfur compounds like dibenzothiophene (DBT) requires severe conditions such as high temperatures and pressures. This results in high desulfurization costs and the circulation of fuels containing high concentrations of sulfur compounds in countries and regions with inadequate desulfurization facilities. As a solution, this study investigated the desulfurization of fuel using visible-light oxidation of DBT catalyzed by commercially available TiO_2 under ambient temperature and pressure conditions.

Through photo-oxidation using model fuels, DBT in the fuel was oxidized to dibenzothiophene-5-oxide (DBTO) and dibenzothiophene-5,5-dioxide (DBTO₂), which were subsequently removed via an extraction process using ethanol. Studies using multiple types of TiO_2 revealed that the anatase-phase catalyst exhibited the highest catalytic activity, achieving >90% of DBT conversion and DBTO₂ yield. Detailed analysis further indicated that the visible light responsiveness of TiO_2 improved within the reaction system, suggesting contributions from the solvent in the model fuel and the resulting oxidized products derived from solvents. Furthermore, as an investigation toward application to commercial fuels, studies using DBT (500 ppm) added gasoline showed a DBTO₂ yield of approximately 40%. However, adding dithranol as an additive at 1 eq relative to DBT improved catalytic activity, achieving the highest DBTO₂ yield of 81% in the studies using gasoline.

1. Introduction

In recent years, research on environmentally friendly clean energy sources such as solar power generation and electric vehicles, along with their utilization, has been advancing worldwide. Meanwhile, aircraft and ships powered primarily by petroleum-derived fuels remain widely used as means of transportation, and demand for fossil fuels remains high. These fossil fuels contain several percent sulfur compounds as impurities. Burning them directly as fuel leads to the generation of sulfur oxides (SO_x), which cause air pollution and acid rain [1-3]. Furthermore, SO_x can cause poisoning of exhaust gas purification catalysts (three-way catalysts) and corrosion of vehicle internal combustion engines [4]. To suppress these problems, desulfurization is performed during the fuel refining process. In Japan and other developed countries today, considering the environmental impact, legal frameworks have been established to limit the sulfur compound concentration in distributed fuels [5-6]. For example, according to the U.S. Environmental Protection Agency's air quality policy requirements, the sulfur compound content in gasoline and diesel fuel must be 10 ppm or less and 15 ppm or less, respectively [7]. In addition, sulfur compound concentrations in marine fuels are regulated by the International Convention for the Prevention of Pollution from Ships (MARPOL), and recent amendments have further tightened these regulations [8]. Furthermore, promoting research on low-environmental-impact fossil fuel technologies is a target to be pursued under the SDGs [9]. In other words, desulfurization technology is indispensable for removing or reducing sulfur compounds in fossil fuels—essential for operating major transportation systems—and making them more environmentally sustainable. Its further development is highly desired.

The current desulfurization method employed is hydrodesulfurization (HDS). This technique uses catalysts containing cobalt or molybdenum species to hydrogenate sulfur compounds, converting them into hydrogen sulfide (H_2S) to achieve desulfurization. Using this method, relatively small sulfur compounds like thiols and thiophenes can be easily desulfurized. However, aromatic sulfur compounds such as benzothiophene and dibenzothiophene (DBT) are large molecules with high stability. Therefore, high-temperature (270–372 °C), high-pressure (50–102 atm of H_2) conditions are required to sufficiently remove them from fuel using the hydrogenation desulfurization method [10–12]. Achieving these conditions poses a challenge in countries and regions lacking desulfurization facilities. Consequently, fuels with sulfur compound concentrations exceeding 500 ppm circulate primarily in African and South American nations (Fig. 1) [13]. In response to this situation, there is a growing demand for developing methods that can easily desulfurize fuels, including aromatic sulfur compounds, under ambient temperature and atmospheric pressure conditions, avoiding harsh reaction conditions.

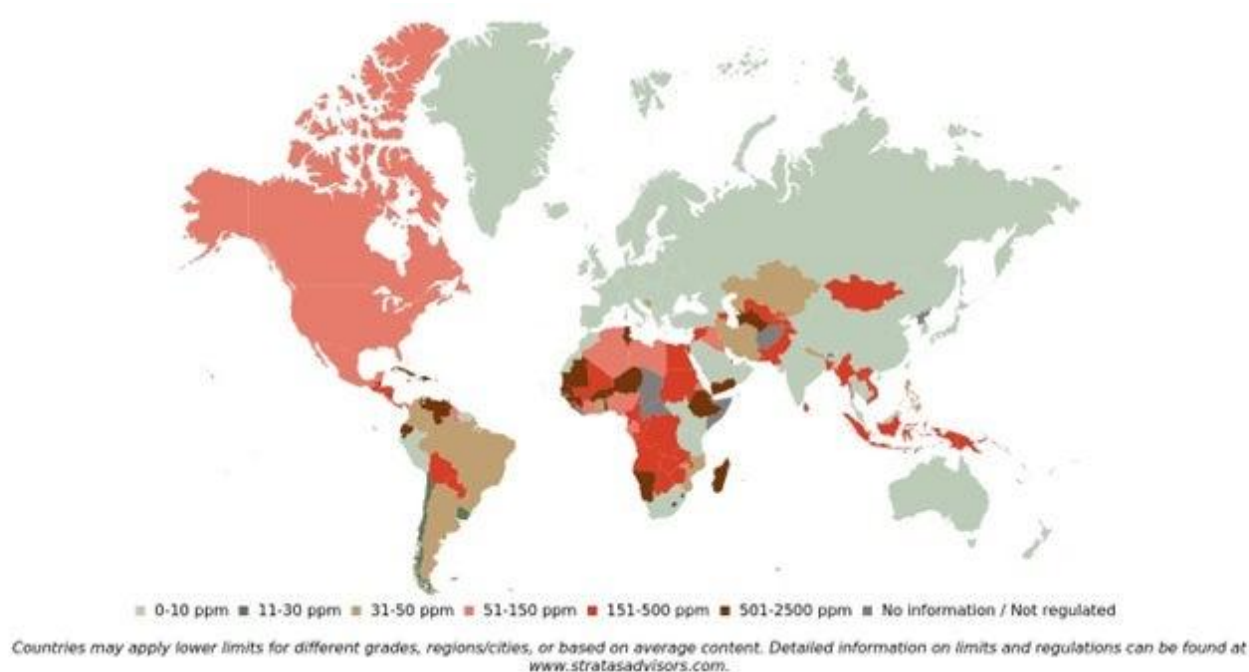


Fig. 1. Limit on sulfur content in gasoline circulated in 2023

(<https://www.stratasadvisors.com/insights/six-countries-move-up-in-top-100-ranking-on-gasoline-sulfur-limits/06222023>)

Development of new desulfurization methods avoiding severe conditions has been ongoing. Examples include oxidative desulfurization (ODS), biodesulfurization (BDS), extractive desulfurization (EDS), and adsorptive desulfurization (ADS). BDS is a technique that removes sulfur compounds from fuels by oxidizing them using microorganisms such as bacteria. Chen *et al.* achieved several DBT derivatives desulfurization from diesel fuel using the hydrophobic bacteria *Gordonia* sp. SC-10 [14]. Glekas et al. reported BDS using *Pseudomonas putida* engineered based on the naturally occurring strain *Rhodococcus qingshengii* IGTS8, which is known to have DBT

degradation activity [15]. ADS is a method that removes sulfur compounds by adsorbing them onto porous materials or onto metals and metal oxides on supports (Fig. 2). Saleh *et al.* reported adsorption desulfurization of aromatic sulfur compounds, including DBT, using manganese oxide supported with activated carbon [16]. They hypothesized that adsorption proceeds via either π -complexation between activated carbon and aromatic rings of sulfur compounds or direct sulfur-metal interactions between sulfur and manganese as the proposed mechanism. Also, Dashtpeyma *et al.* reported ADS using nickel and cerium doped mesoporous NaY zeolite prepared via dealumination and desilication, achieving moderate DBT removal from DBT (1000 ppm) contained model fuel [4, 7]. Additionally, Sun *et al.* reported the adsorption desulfurization of DBT using titanium oxide supported with silver nanoparticles, confirming that desulfurization efficiency improves when adsorption is performed under ultraviolet (UV) light irradiation [17]. They speculated that ultraviolet irradiation of the catalyst in the presence of water led to an increase in the number of Ti (IV)-OH sites, which positively contributed to the adsorption desulfurization process. However, these methods face the challenge that while they can sufficiently desulfurize moderate-concentration sulfur compounds less than 1000 ppm, they do not function adequately under higher concentration conditions. Furthermore, while EDS uses ionic liquids [18] or deep eutectic solvents [19] to remove sulfur compounds from fuel, their reuse requires several steps, posing problems in terms of desulfurization efficiency. On the other hand, ODS converts sulfur compounds in fuel into sulfoxides or sulfones via oxidation reactions. With DBT, it converts to dibenzothiophene-5-oxide (DBTO) or dibenzothiophene-5,5-dioxide (DBTO₂). These compounds readily dissolve in solvents immiscible with fuel oil, such as acetonitrile, allowing for easy extraction and removal. Therefore, desulfurization can be completed by

performing an extraction process after the oxidation reaction. Furthermore, this method enables desulfurization with high reaction efficiency even in fuels with several hundred ppm or more of sulfur compounds, making it a viable alternative to current methods. However, ODS requires heating to approximately 60–70 °C to promote the reaction [20–21]. Therefore, the photo-oxidative desulfurization (PODS) was developed to enable the process under ambient conditions by utilizing photochemical reactions rather than thermal reactions for the oxidation of sulfur compounds. This technique has recently gained attention as a desulfurization method that can be performed under mild conditions using photocatalysts.

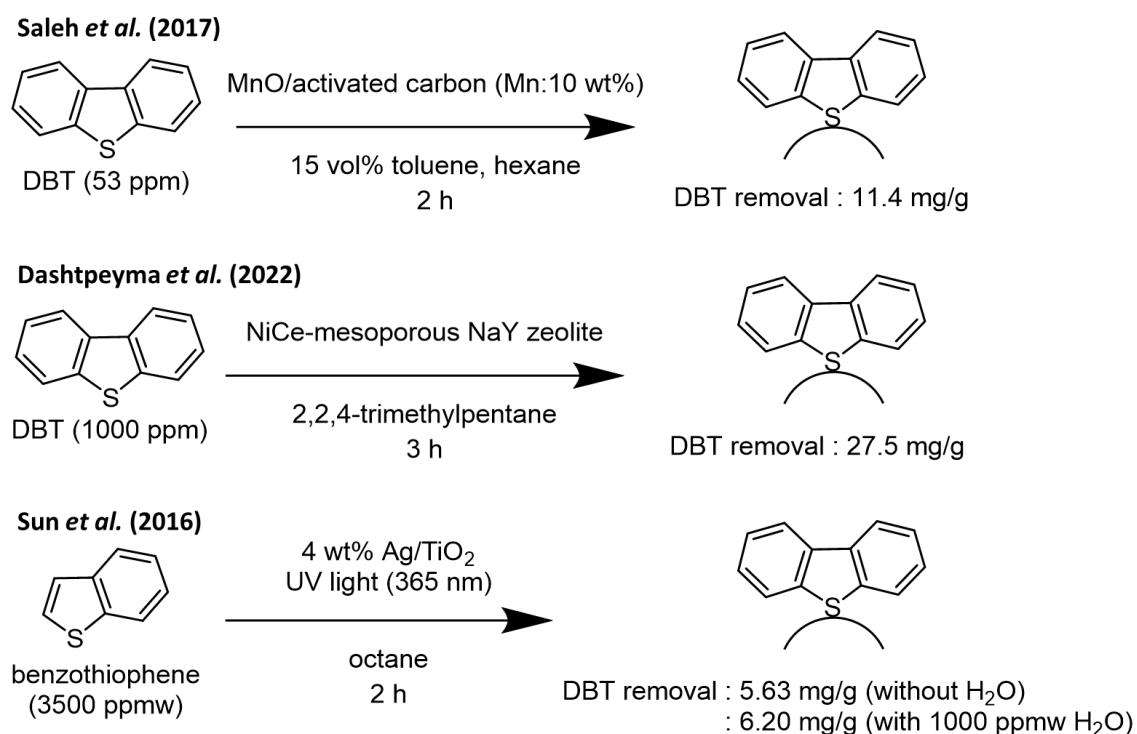
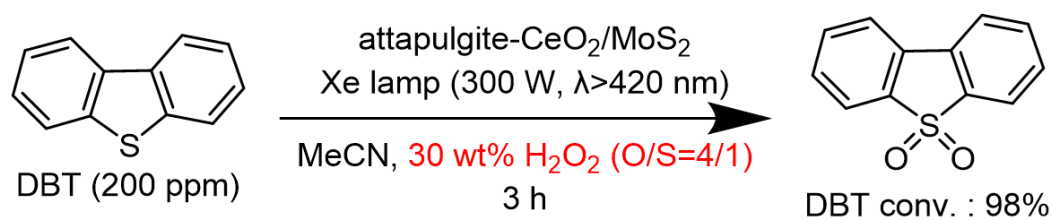


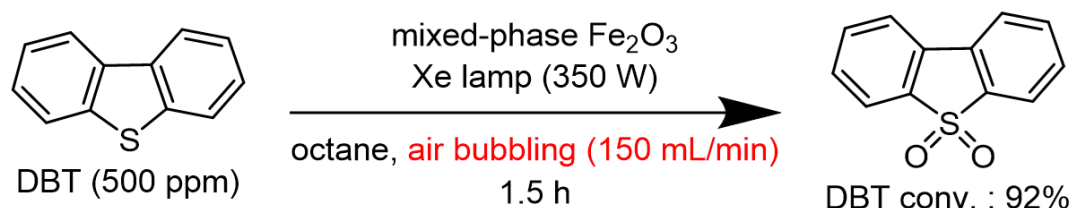
Fig. 2. Previous reports of ADS

Various types of catalysts for PODS have been studied, such as AgCl/PbMoO₄ [22], atapaljtite-CeO₂/MoS₂ [23], BiOBr-C₃N₄/MCM-41 [24], CdSe/rGO [25], Fe₃O₄@SiO₂/Bi₂WO₆/Bi₂S₃ [26], MoO₃-TMU-5 [27], and numerous other catalysts. Notably, Ti-based species such as Au-*m*-TiO₂/g-C₃N₄ [28], Ca(CO₃)TiO₂ [29], Ce/MIL-125-NH₂ (Ti MOF) [30], Cu/C-TiO₂ [31], and Cu-TiO₂/BiVO₄ [32] are widely employed as photocatalysts and catalyst supports for desulfurization. However, there are still unresolved challenges, and it has not yet reached the stage of practical application (Fig. 3). Lu *et al.* detailed the preparation and desulfurization evaluation of inexpensive, efficient, and environmentally friendly N-doped CeO₂-TiO₂ nanosheets [33]. Wang *et al.* successfully removed high concentrations of DBT (500 ppm) from acetonitrile using TiO₂/g-C₃N₄ [34]. While these studies achieve high DBT conversion in relatively short times, they also face the issue of requiring hydrogen peroxide, a highly dangerous and strong oxidant, which must be used in excess relative to the sulfur compound concentration in the model fuel. Additionally, some examples use oxygen or air bubbling instead of hydrogen peroxide, although this approach is disadvantageous due to the need for additional equipment [35-38]. Li *et al.* reported PODS under air conditions without requiring excess oxidants or oxygen gas; however, the target compound was solely thiophene, and DBT derivatives were not verified [39]. To address this challenge, the author investigated DBT photo-oxidation that utilizes atmospheric oxygen or dissolved oxygen in fuel as the oxidant.

a) Requiring excessive amount of strong oxidant (Li *et al.*, 2016)



b) Additional facility for gas bubbling (Li *et al.*, 2012)



c) Almost no reports of PODS under ambient air (Li *et al.*, 2020)

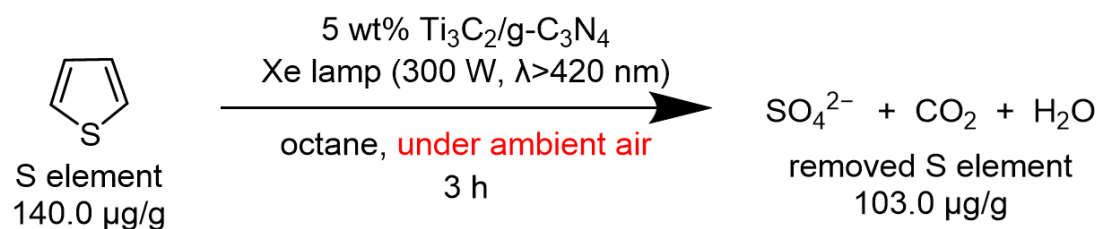


Fig. 3. Unresolved challenges for the practical application of PODS

As a photochemical desulfurization method, techniques that liberate only sulfur atoms from sulfur compounds are conceivable. Previous studies have predicted that irradiating thiophene and dibenzothiophene derivatives with a xenon lamp can remove only sulfur atoms through the cleavage of carbon-sulfur bonds [40-41]. Furthermore, Shinozaki *et al.* have reported that UV irradiation of benzothiophene and dibenzothiophene decomposes sulfur compounds into elemental sulfur and hydrocarbons [42]. If applicable, this method could serve as a simple new desulfurization technique proceeding solely by light irradiation, potentially replacing current methods. However, fuels like gasoline contain numerous aromatic hydrocarbons that absorb UV light, inhibiting the UV absorption of

sulfur compounds within the fuel (Fig. 4). To avoid this inhibition, the driving force for the photoreaction needs to be long-wavelength light that does not overlap with the absorption region of aromatic compounds. According to the research of Higashimoto 's group, it has been reported that the visible light absorption of titanium dioxide, which normally does not exhibit visible light responsiveness, increases when toluene or benzyl alcohol interacts with its surface [43-45]. Based on these reports, the author considered that using titanium dioxide as a catalyst would enhance its visible-light responsiveness due to the aromatic hydrocarbons in the fuel, thereby enabling PODS to use visible light irradiation.

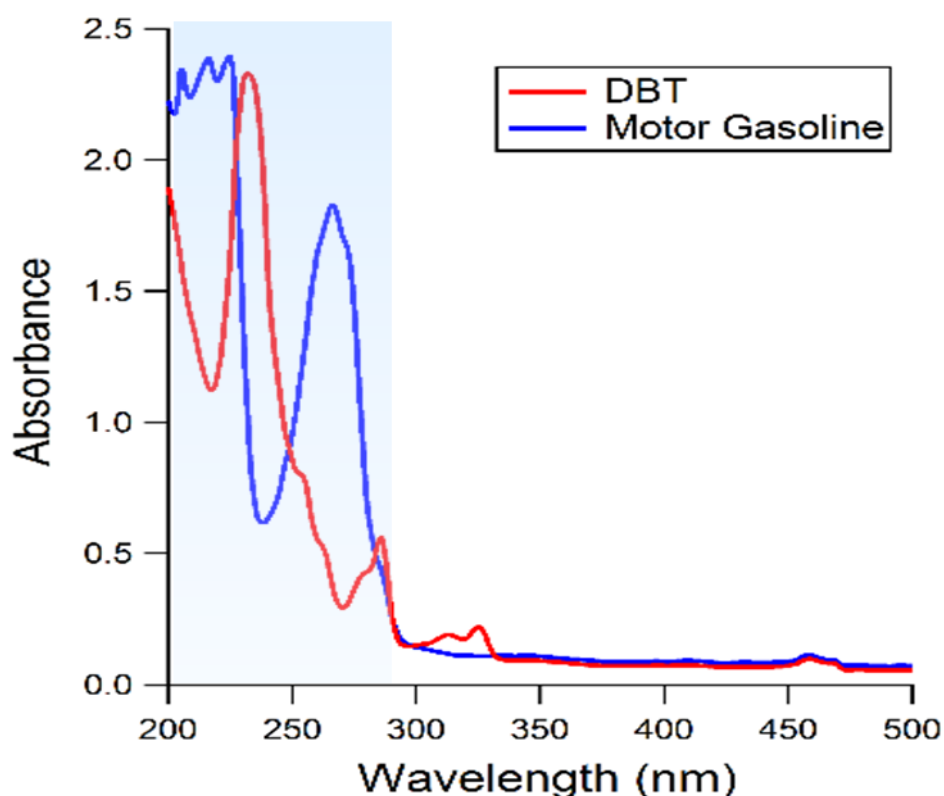


Fig. 4. UV-vis spectra of DBT and motor gasoline. The blue area is the overlap between the absorbance of DBT and the absorbance of aromatic compounds in gasoline.

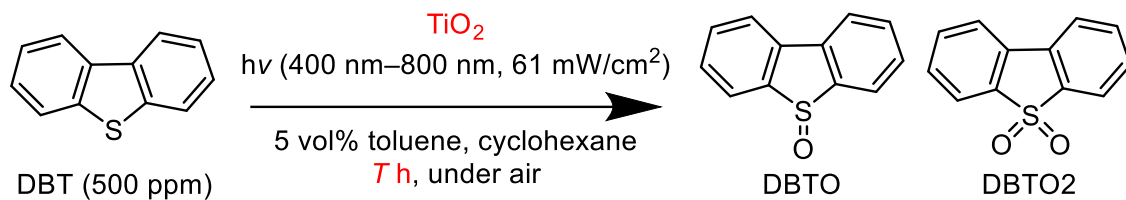
In this study, the author investigated the desulfurization of dibenzothiophene via photo-oxidation using visible light. Using TiO_2 as the catalyst, high DBT conversion and DBTO₂ yield were achieved, particularly when using anatase-phase TiO_2 . Furthermore, UV-visible (UV-vis) absorption spectra revealed visible light absorption of the used catalyst. To identify the cause, various conditions were investigated. The results suggest that toluene and cyclohexane contained in the model fuel, or compounds formed by the oxidation of these solvents, contribute to the visible light absorption exhibited by the catalyst. Additionally, studies were conducted to explore even more highly active catalyst systems, identifying reaction conditions that exhibit high activity even under severe conditions, such as model fuels containing DBT (1000 ppm) and DBT (500 ppm)-added commercial gasoline.

2. Results and discussion

2.1. Exploring conditions of DBT photo-oxidation

The author conducted photo-oxidation catalyzed by TiO_2 using a model fuel (DBT 500 ppm) to determine reaction conditions. Four types of TiO_2 , ST-01 (anatase-phase), JRC-TIO-10 (anatase-phase), P-25 (a mixture of anatase and rutile-phase), and STR-100N (rutile-phase) were used as catalysts. Using ST-01 and JRC-TIO-10, the author achieved high DBT conversions (83% and 82%) and DBTO₂ yields (70% and 63%) in 4 h reactions (Table 1, entries 1 and 4). In contrast, the catalytic activities of P-25 and STR-100N were low. For P-25, DBT conversion was 34%, and DBTO₂ yield was 16%, respectively; corresponding results of STR-100N were 23% and 5% (entries 7 and 8). From these results, anatase-phase TiO_2 was considered appropriate for this reaction. Also, the author investigated that the photo-oxidation did not proceed under catalyst-free and dark conditions (entries 9 and 10). These results showed that TiO_2 and light irradiation were essential for this photo-oxidation. In addition, the author conducted a study of reaction time (T) using anatase-phase TiO_2 with high catalytic activities. Whichever anatase-phase TiO_2 was used, the conversion rate and yield were improved as the reaction time was extended. Especially when using JRC-TIO-10 for an 8 h reaction, the DBTO₂ yield reached a maximum of 92% (entry 6). Based on these results, it was determined that an 8 h reaction using anatase-phase TiO_2 is most suitable for this photo-oxidation.

Table 1. Study of reaction conditions



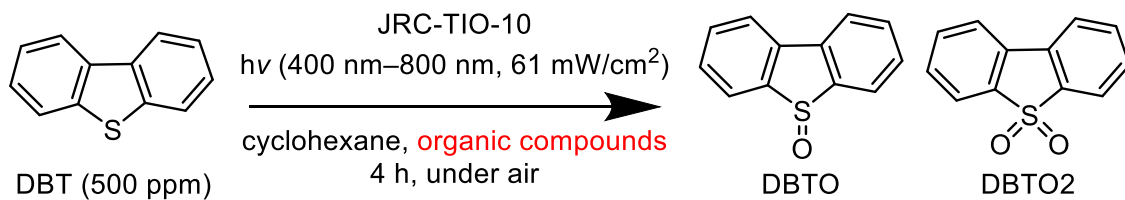
Entry	TiO ₂	<i>T</i> (h)	Conv. (%)	DBTO (%)	DBTO2 (%)
1	ST-01	4	83	4	70
2	ST-01	6	99	0	68
3	ST-01	8	97	0	78
4	JRC-TIO-10	4	95	0	76
5	JRC-TIO-10	6	97	0	84
6	JRC-TIO-10	8	>99	0	92
7	P-25	4	34	0	16
8	STR-100N	4	23	1	5
9	—	4	25	0	0
10 ^a	JRC-TIO-10	4	14	0	1

^a dark condition

2.2. Effects of co-existing organic compounds

In order to reproduce conditions closer to actual fuels, toluene was added to the model fuel together with cyclohexane used as a solvent. To investigate whether this toluene affects catalyst activity, a study was conducted on the concentration of toluene contained in the model fuel. JRC-TIO-10 was used as the catalyst, and DBT photo-oxidation was carried out for 4 h. DBT conversion rate was 82% and DBTO₂ yield was 68% for the model fuel containing toluene (5 vol%) (Table 2, entry 2). Without toluene, however, the conversion rate dropped to 74%, and the DBTO₂ yield to 53% (entry 1). Furthermore, when the toluene concentration was raised to 10 vol%, the DBT conversion increased to 94% and the DBTO₂ yield to 86% (entry 3). The author also examined the effect of adding 1 μ L of toluene (1.2 eq to DBT), which resulted in an improved yield compared to the toluene-free condition (entry 4). From these results, it was indicated that the toluene concentration in the model fuel affected the photo-oxidation activity of the catalysts. Additionally, the author also investigated the addition of organic compounds that could originate from toluene or cyclohexane. There were four types of organic compounds examined: benzyl alcohol, benzaldehyde, cyclohexanol, and cyclohexanone, each added at 1 μ L (1.2 eq to DBT). As a result, DBT conversion and DBTO₂ yield improved in all cases compared to the toluene-free condition (entries 5–8). Especially when adding benzyl alcohol or benzaldehyde, high activity exceeding 99% was achieved for both conversion and yield. These results indicate that not only toluene but also organic compounds that can be generated by the photo-oxidation of solvent molecules influence the catalytic activity.

Table 2. Study of co-existing organic compounds



Entry	Organic compounds	Amount	Conv. (%)	DBTO (%)	DBTO2 (%)
1	—	—	74	6	53
2	Toluene	5 vol%	95	0	76
3	Toluene	10 vol%	94	0	86
4	Toluene	1 μ L	92	0	58
5	Benzyl alcohol	1 μ L	99	0	99
6	Benzaldehyde	1 μ L	99	0	>99
7	Cyclohexanol	1 μ L	86	0	74
8	Cyclohexanone	1 μ L	85	0	62

2.3. Photo-oxidation mechanism

2.3.1. Characterization of fresh and used catalysts

Fresh JRC-TIO-10 and JRC-TIO-10 after 8 h DBT photo-oxidation were characterized by various methods. Fig. 5 shows the XRD patterns of these catalysts. Diffraction peaks of fresh catalyst were observed at 25.3, 37.8, 47.9, 54.6 (broad peak), and 62.6°. Also, diffraction peaks of the used catalyst were observed at 25.3, 37.8, 48.0, 54.5 (broad peak), and 62.6°. Each catalyst exhibited peak characteristics typical of anatase-phase TiO₂ [46]. Furthermore, there was little change before and after the photo-oxidation, suggesting that structural changes of the catalyst did not occur significantly during the reaction. The FT-IR spectra of the catalysts were measured using attenuated total reflection (ATR). As shown in Fig. 6, no significant spectral changes were observed in either the fresh or used catalysts, with only a slight peak detected at 1635 cm⁻¹ corresponding to the Ti-OH stretching vibration [47]. UV-vis spectra of each catalyst were obtained using the diffuse reflectance method. (Fig. 7 (a)). The spectrum indicated by the red line revealed that the fresh catalyst exhibits no significant absorption in the visible region above 400 nm. However, the used catalyst, indicated by the blue line, showed absorption in the 400 nm to 600 nm region. According to previous reports, absorption was observed in the range of $\lambda = 420\text{--}540$ nm in the absorption spectrum of toluene-adsorbed TiO₂, consistent with the results of this measurement [43]. It is also consistent with the result that the fresh catalyst was white, whereas it had turned yellow after the photo-oxidation. Moreover, when the spectrum of the catalyst irradiated with visible light for 1 h in toluene or cyclohexane was measured, absorption in the 400 nm to 600 nm range was confirmed, similar to the used catalyst (yellow and green lines in Fig. 7 (a)). These suggest that visible light absorption

of TiO_2 increases during the reaction process. Additionally, based on the measured diffuse reflectance spectra, a Tauc plot was created, and the bandgap energy was calculated (Fig. 7 (b)). Table 3 shows the estimated bandgap energy, the valence band (VB), and the conduction band (CB) energies derived from it. These energy values showed little change before and after the reaction.

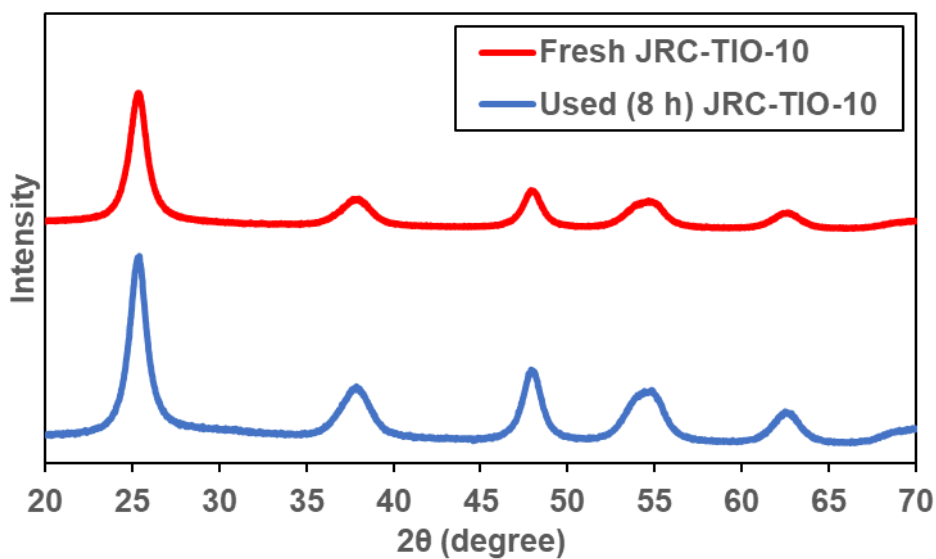


Fig. 5. XRD patterns of fresh (red) and used 8 h (blue) catalysts

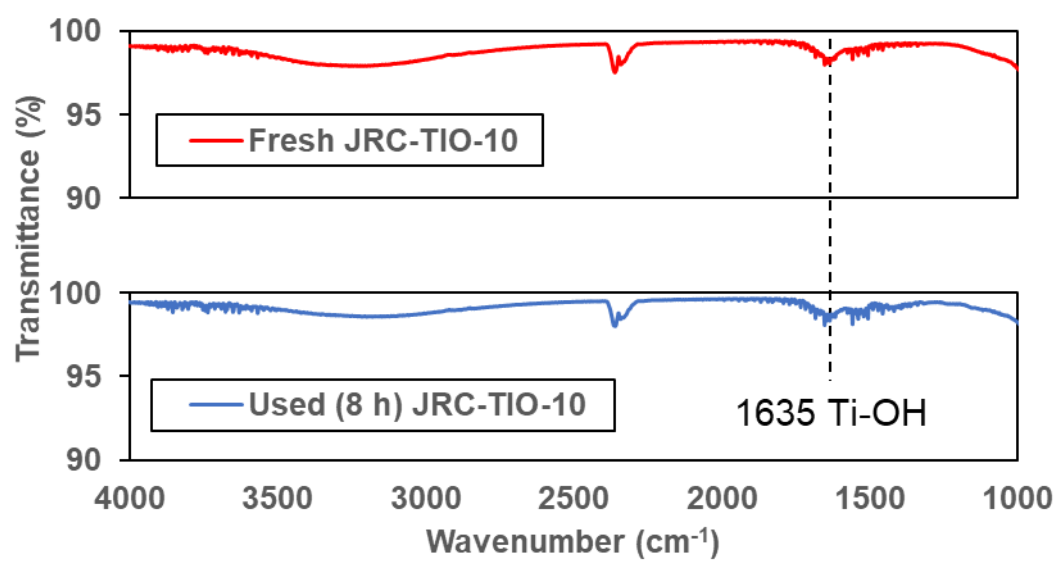
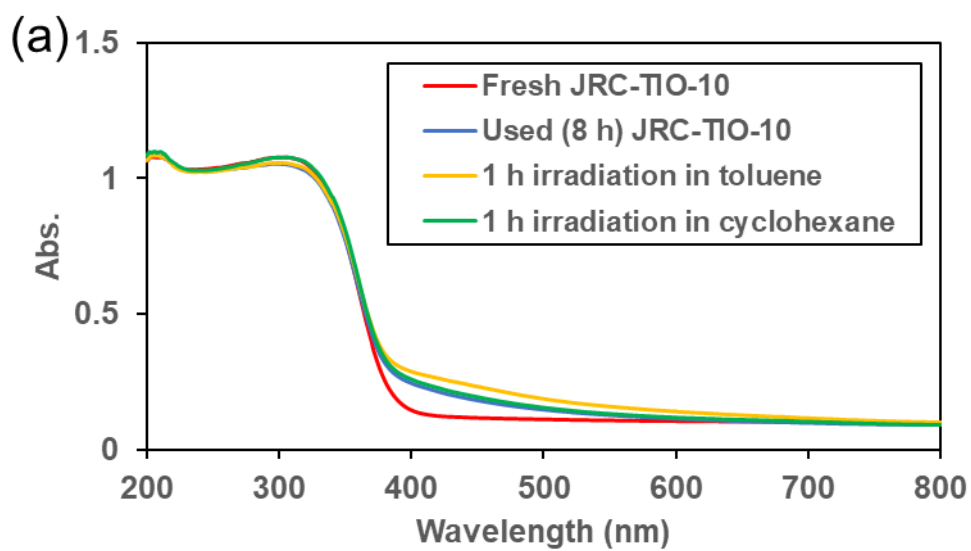


Fig. 6. FT-IR spectra of fresh and used 8 h catalysts



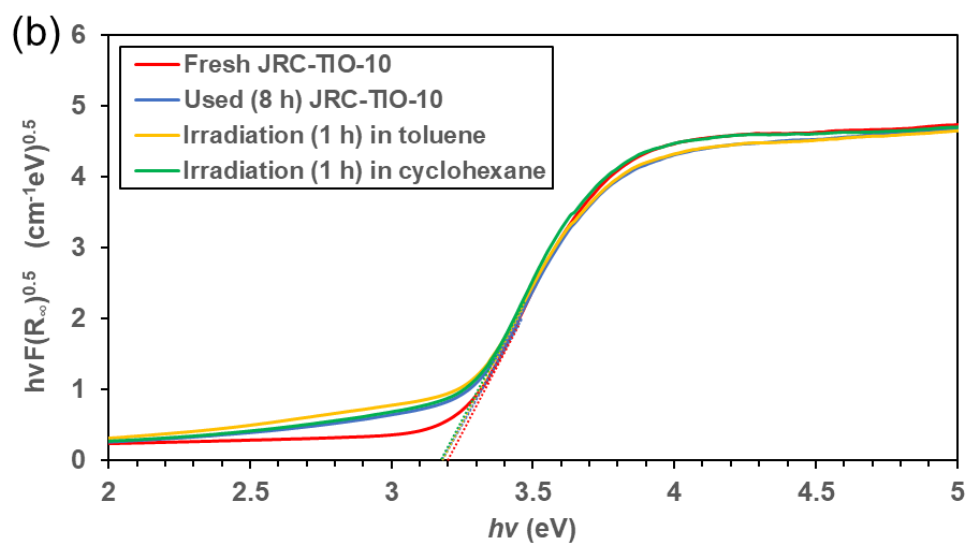


Fig. 7. (a) UV-vis spectra of catalysts, (b) Tauc plot of each catalyst. The dotted lines represent the extrapolated linear segments in each Tauc plot, and their intersection points with the energy axis correspond to the determined bandgap energies.

Table 3. Bandgap energy of JRC-TiO-10 catalysts

Entry	Catalyst conditions	E_g (eV)	E_{VB} (eV)	E_{CB} (eV)
1	Fresh	3.20	2.91	-0.29
2	Used 8 h reaction	3.17	2.90	-0.28
3	Irradiated 1 h in toluene	3.17	2.90	-0.28
4	Irradiated 1 h in cyclohexane	3.17	2.90	-0.28

2.3.2. Analysis in the initial stage of photo-oxidation

To compare the activity differences between the anatase-phase (JRC-TIO-10) and rutile-phase (STR-100N) catalysts in detail, apparent reaction rate constants (k_{app}) were calculated using pseudo-first-order plots based on the amount of DBT converted during the initial reaction stage (0–2 h) (Fig. 8). The results showed that STR-100N had a value of 0.0012 (min^{-1}), whereas JRC-TIO-10 exhibited a value of 0.0052 (min^{-1}), approximately 4.3 times higher. Two factors could account for this difference in reaction rates. One possibility is the difference in specific surface area. While STR-100N has a BET specific surface area of 77 m^2/g , JRC-TIO-10 has a specific surface area of 243 m^2/g , approximately 3.2 times larger, which could lead to differences in catalytic activity. Another possibility is a difference in the lifetime of photoexcited carriers due to the crystalline phase. According to research by Ozawa *et al.*, it has been experimentally confirmed that the lifetime of carriers generated by photoexcitation is longer in the anatase phase compared to the rutile phase [48]. Therefore, anatase titanium dioxide may allow for a longer time before the recombination of electrons and holes generated by photoexcitation, potentially enabling a more efficient photocatalytic reaction.

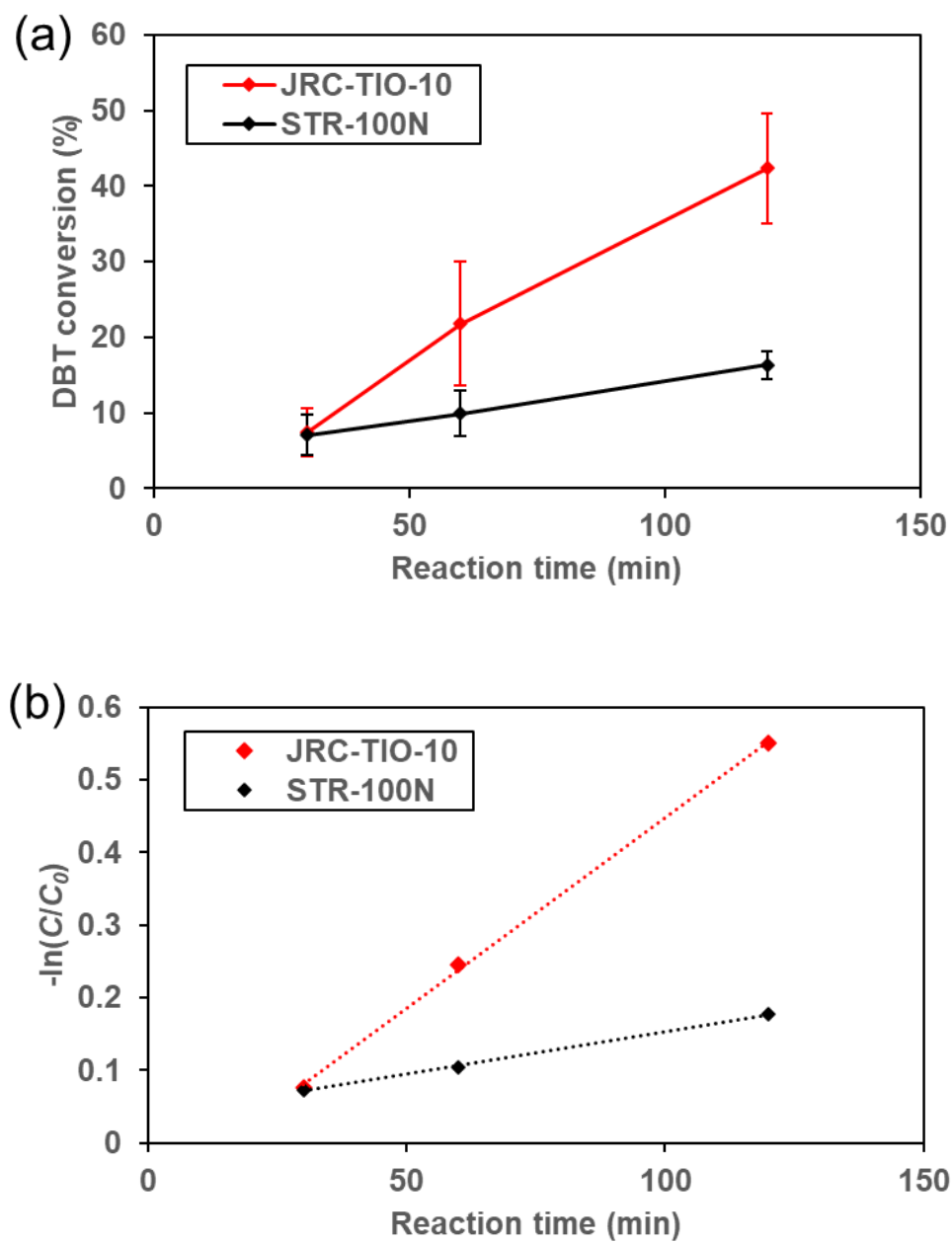
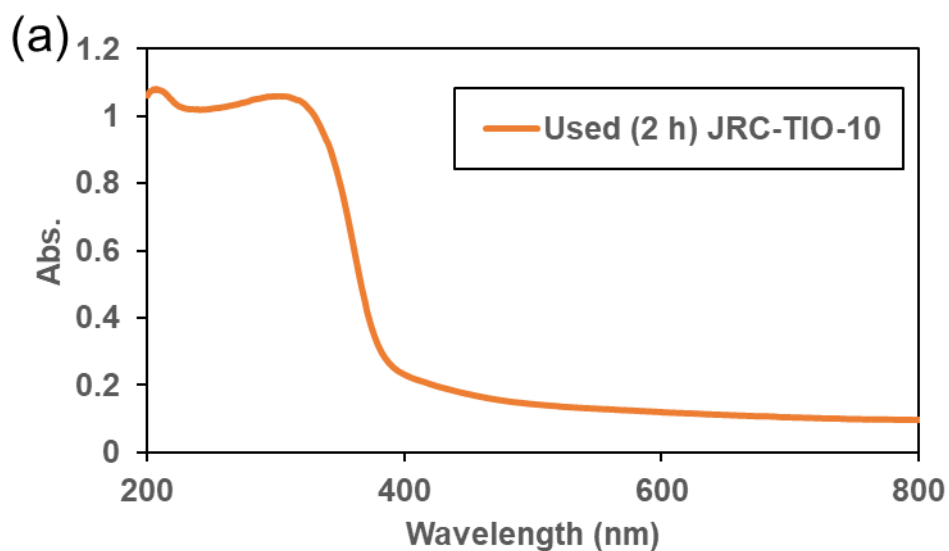


Fig. 8. (a) Timeline of DBT conversion. Average values of DBT conversion are shown with the standard deviation of the measured data as error bars. (b) Pseudo-first-order plots.

Additionally, the UV-vis spectrum of the used JRC-TIO-10 after 2 h photo-oxidation was obtained. As shown in Fig. 9 (a), it was confirmed that the visible light absorption of the catalyst had already increased within the first 2 h after the reaction started. Furthermore, a Tauc plot (Fig. 9 (b)) was constructed based on the measured values, and the calculated bandgap energy was 3.17 eV, which was confirmed to be comparable to that of the catalyst after 8 h reaction.



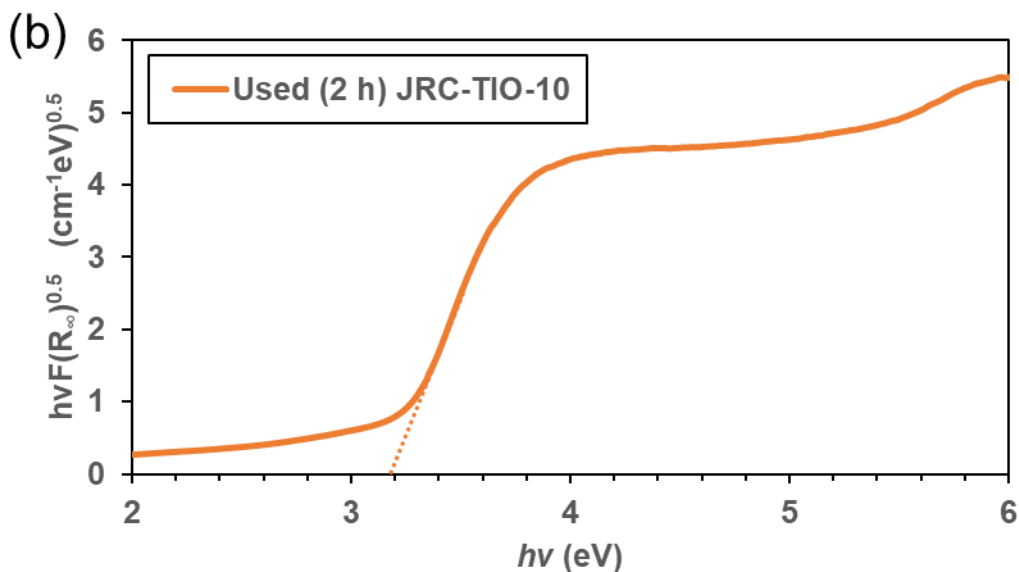


Fig. 9. (a) UV-vis spectrum of the used 2 h catalyst, (b) Tauc plot of the used 2 h catalyst. The dotted lines represent the extrapolated linear segments in each Tauc plot, and their intersection points with the energy axis correspond to the determined bandgap energies.

2.3.3. External quantum yield of photo-oxidation

To evaluate this photo-oxidation, the external quantum yield (ϕ_{ex}) was estimated. This value was obtained by calculating the number of photons irradiated per hour during experiments using monochromatic light LEDs and the number of DBT molecules consumed up to that time. Then, the author examined four types of LED lamps with wavelengths of 430 nm, 455 nm, 470 nm, and 505 nm. As shown in Fig. 10, the ϕ_{ex} values were 1.5×10^{-1} (430 nm), 2.3×10^{-2} (455 nm), 7.3×10^{-3} (470 nm), and 2.6×10^{-2} (505 nm). The value of ϕ_{ex} decreased as the wavelength of the LED light used became longer.

Furthermore, this result was in agreement with the absorption trend observed in the UV-vis spectrum of the used catalyst (Fig. 11).

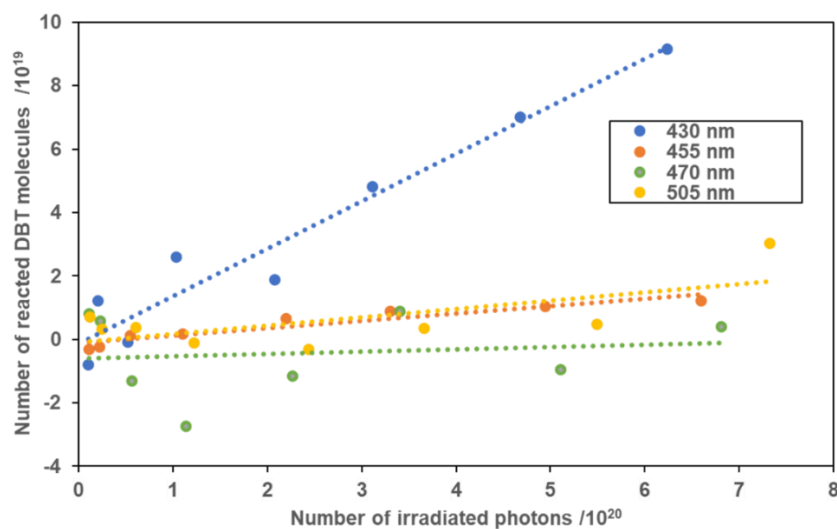


Fig. 10. Number of reacted DBT molecules versus number of exposed photons.

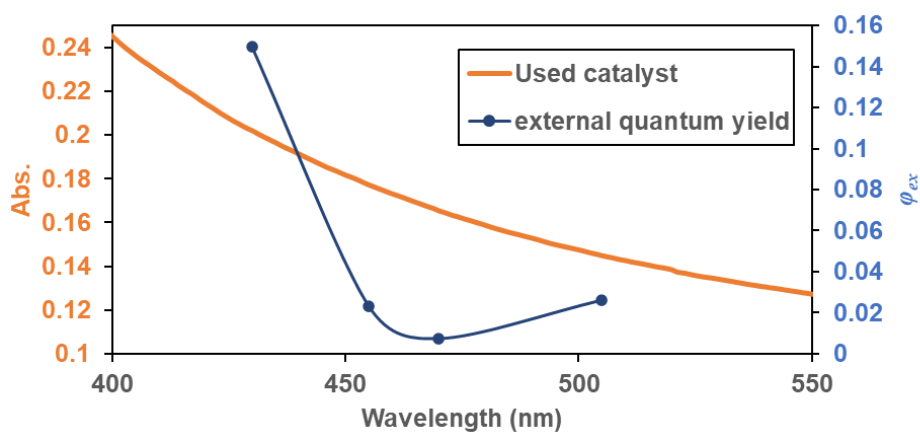


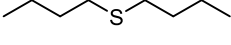
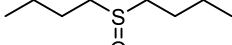
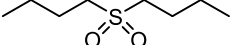
Fig. 11. Action spectra. Blue line: the plot of external quantum yield.

Orange line: UV-vis spectrum of Used (8 h) JRC-TIO-10.

2.3.4. Further study for mechanism estimation

The TiO₂-catalyzed photo-oxidation was studied using dibutyl sulfide (DBSF) as the substrate. As a result, the conversion of DBSF in the 4 h reaction was 95%, the yield of dibutyl sulfoxide (DBSFO) and dibutyl sulfone (DBSFO₂) as the oxidized products were 30% and 73%, respectively (entry 1, Table 4). Furthermore, the UV-vis spectrum of the catalyst used in this reaction (Fig. 12 (a)) revealed increased absorption in the 400–600 nm region, consistent with the results obtained using DBT. A Tauc plot (Fig. 12 (b)) was constructed based on these measurements to calculate the bandgap energy, yielding a value of 3.17 eV, comparable to other used catalysts. In addition, it confirmed that visible-light oxidation of DBSF did not proceed under dark conditions or under non-catalyst conditions. These results demonstrated that this method applies not only to DBT but also to other sulfur compounds, and suggested that DBT is not involved in the activation of the catalyst during the photo-oxidation.

Table 4. DBSF photo-oxidation

 DBSF (500 ppm, 3.4 mmol/L) $\xrightarrow[\text{5 vol\% toluene, cyclohexane, 4 h, under air}]{\text{JRC-TiO-10, } h\nu \text{ (400 nm–800 nm, 61 mW/cm}^2\text{)}}$  DBSFO  DBSFO₂				
Entry	TiO ₂	Conv. (%)	DBSFO (%)	DBSFO ₂ (%)
1	JRC-TiO-10	95	30	73
2 ^a	JRC-TiO-10	0	0	0
3	—	5	0	0

^a dark condition

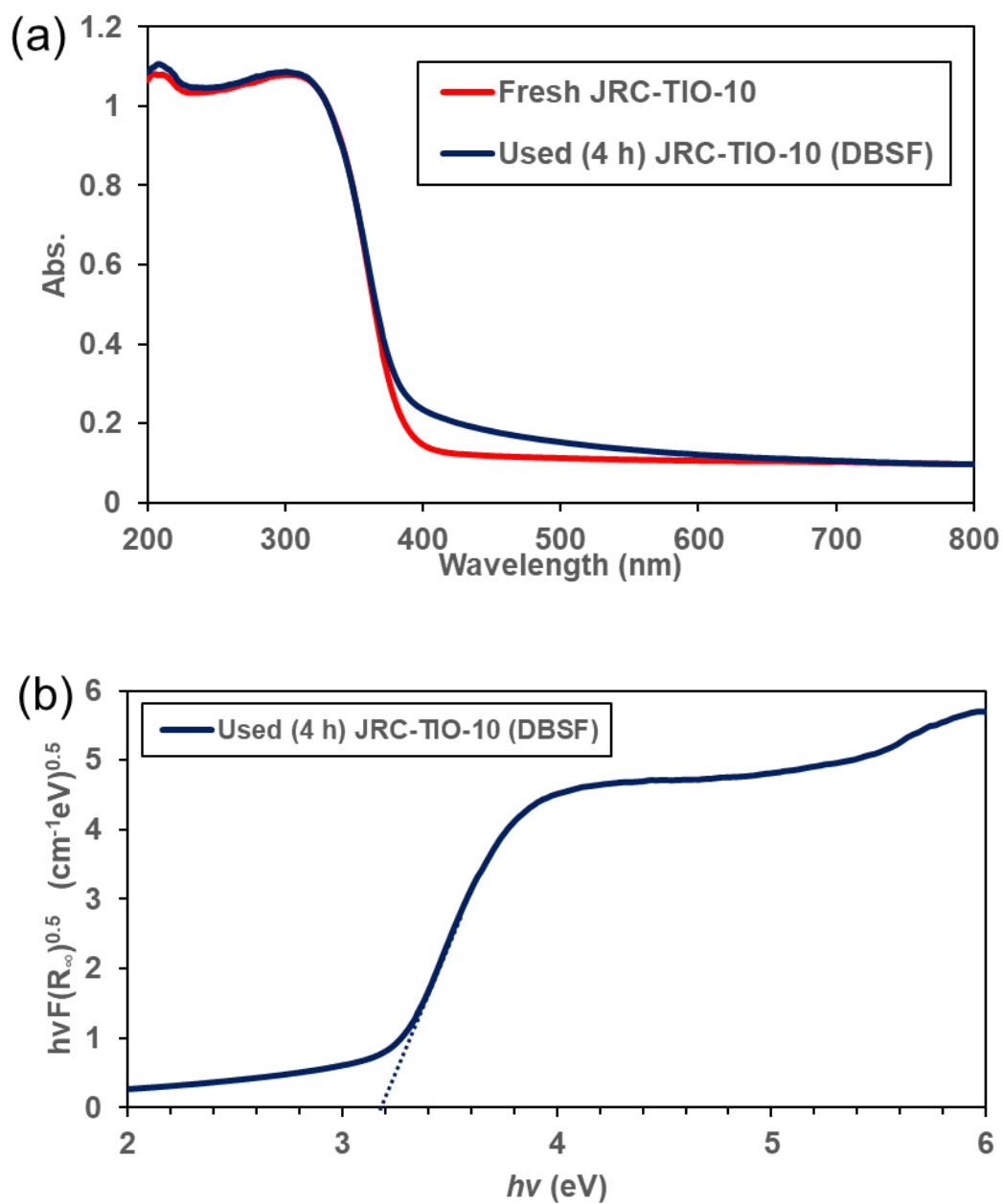
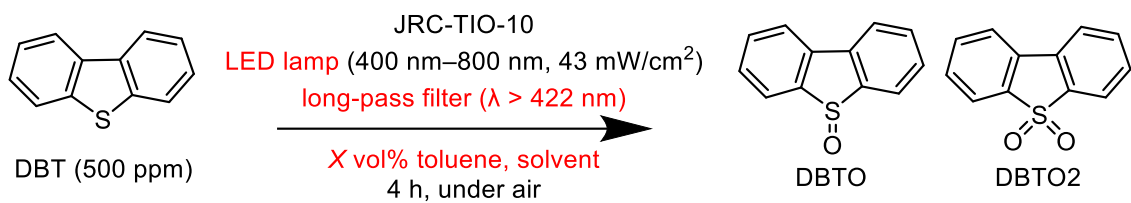


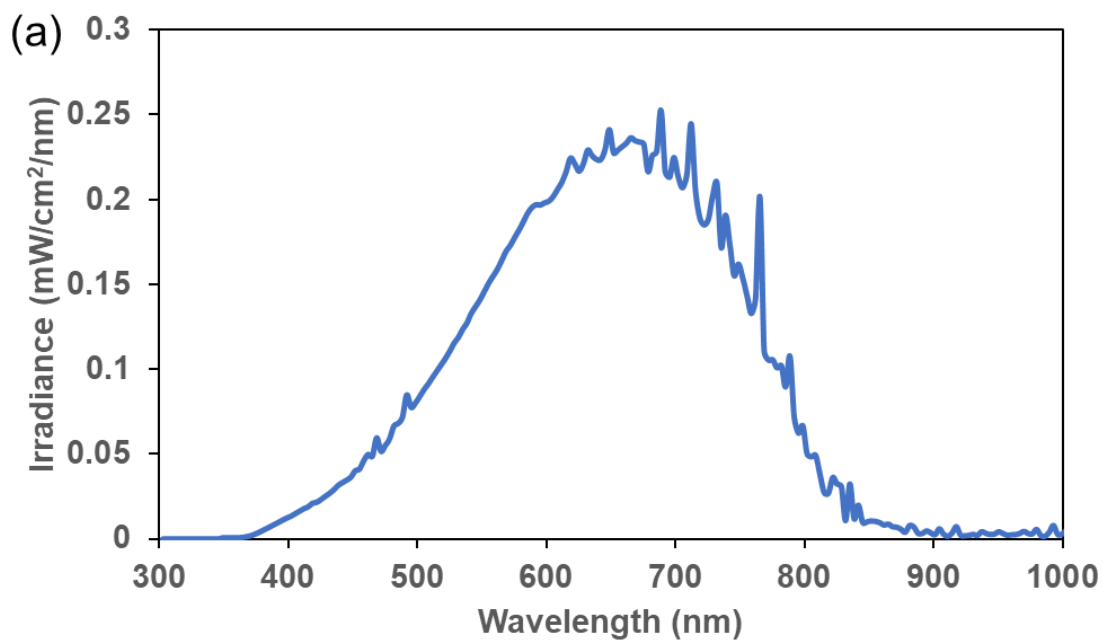
Fig. 12. (a) UV-vis spectrum of the catalyst used in DBSF photo-oxidation (4 h), (b) Tauc plot of the catalyst used in DBSF photo-oxidation (4 h). The dotted lines represent the extrapolated linear segments in each Tauc plot, and their intersection points with the energy axis correspond to the determined bandgap energies.

Besides, the author conducted studies using a white LED with a filter as the light source instead of conventional halogen lamps. A filter that transmits only visible light ($\lambda > 422$ nm) was used. When studied under conditions containing 5 vol% toluene or without toluene, the yields of DBTO₂ were 17% and 10%, respectively, with cyclohexane as the solvent (entries 1 and 2, Table 5). Considering the light source spectrum (Fig. 13), switching to a white LED equipped with a filter resulted in a decrease in DBT conversion efficiency and DBTO₂ yield. This difference was attributed to the lower light intensity of the filtered white LED (43 mW/cm²) compared to the halogen lamp (61 mW/cm²), which also contained a small amount of ultraviolet light below 400 nm. The filtered white LED only emitted visible light ($\lambda > 422$ nm). Thus, these results suggested that this reaction proceeds even under visible light alone. Also, to verify the catalytic activity when replacing the solvent, hexane was used as the solvent under the same conditions. In the solution containing 5 vol% toluene, the DBTO₂ yield was 20%, while in the toluene-free solution, it was 2% (entries 3 and 4). The study using hexane suggested that toluene or cyclohexane was necessary for the efficient progression of this reaction, indicating that these organic compounds were involved in the activation of the catalyst.

Table 5. Study using a white LED and a long-pass filter ($\lambda > 422$ nm)



Entry	Solvent	Toluene (vol%)	Conv. (%)	DBTO (%)	DBTO2 (%)
1	Cyclohexane	0	47	1>	10
2	Cyclohexane	5	57	0	17
3	Hexane	0	42	0	2
4	Hexane	5	50	0	20



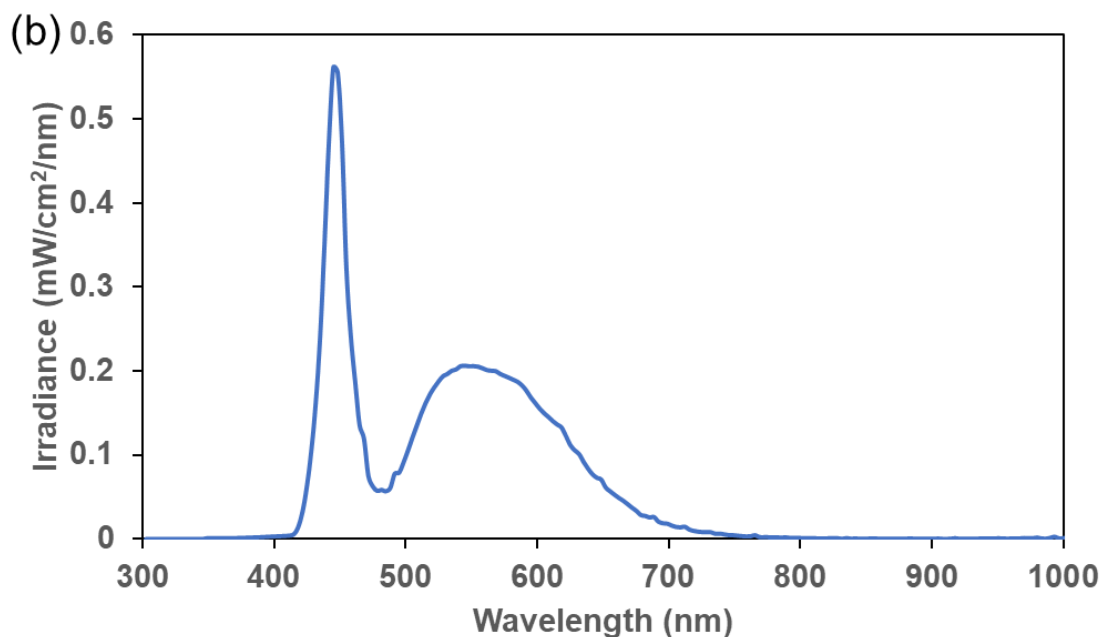
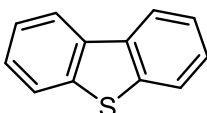
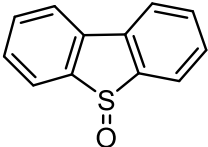
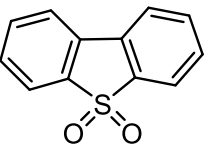


Fig. 13. The spectra of light sources (a) Halogen lamp (b) White LED with long-pass filter ($\lambda > 422$ nm)

To identify the oxygen radical species involved in this photo-oxidation, radical trapping experiments were conducted. The experiment was conducted using model fuel (DBT 500 ppm), with a radical scavenger added at approximately 1 eq relative to DBT (mole). As radical scavengers, 1,4-benzoquinone (1,4-BQ), which was the scavenger for superoxide anion radical ($\cdot\text{O}_2^-$), and dimethyl sulfoxide (DMSO), which was the scavenger for hydroxyl radical ($\cdot\text{OH}$), were used. The radical trapping experiment results are shown in Table 6. When 1,4-BQ (1 eq) was used, the conversion was 43%, and the DBTO₂ yield was 17% (entry 2). On the other hand, with DMSO (1.7 eq), the conversion rate was 15%, and the DBTO₂ yield was 6% (entry 5). Regardless of which scavenger was used, both the DBT conversion and DBTO₂ yield decreased compared to the case without any scavenger added. Furthermore, the DBTO₂ yield decreased as the added amount of

radical scavenger increased, revealing a negative correlation between them. Therefore, oxygen radicals were involved in this reaction. Since a greater decrease in conversion and yield was observed when DMSO was used, this suggested that $\cdot\text{OH}$ is primarily involved in the reaction.

Table 6. Oxygen radical trapping experiments

 DBT (500 ppm) JRC-TIO-10 $h\nu$ (400 nm–800 nm, 61 mW/cm²) 5 vol% toluene, cyclohexane radical scavenger 4 h, under air  DBTO  DBTO2				
Entry	Scavengers (amount)	Conv. (%)	DBTO (%)	DBTO2 (%)
1	1,4-BQ (0.5 eq)	75	0	53
2	1,4-BQ (1 eq)	43	1	17
3	1,4-BQ (2 eq)	36	8	14
4	DMSO (0.9 eq)	48	6	34
5	DMSO (1.7 eq)	15	3	6
6	DMSO (3.4 eq)	14	0	3

2.3.5. Possible mechanism

Fig. 14 shows the proposed reaction mechanism. Based on the experimental results obtained thus far, the author considered that there was an activation step in the initial stage of photo-oxidation where the visible-light responsiveness of the catalyst was enhanced. Furthermore, during this activation, solvents such as toluene in the model fuel and oxidized products derived from these solvents were likely involved. According to previous studies, it has been reported that in the catalytic photo-oxidation of toluene and benzyl alcohol, the interaction of these compounds with TiO_2 increases the visible light absorption of the catalyst [43-45]. In particular, for the photooxidation of benzyl alcohol, it has been proposed that OH- π interactions and hydrogen bonding between hydroxyl groups—involving the π electrons of the aromatic ring and the hydroxyl group of benzyl alcohol with the hydroxyl groups on the titanium dioxide surface—contribute to the increased visible light absorption of the catalyst. Additionally, it has been reported that modifying the Pt/ TiO_2 surface with 2,3-dihydroxynaphthalene (2,3-DN) enhances the visible light absorption and photocatalytic reduction activity [49]. In this study, 2,3-DN was presumed to modify the titanium oxide surface by forming complexes through a mechanism involving dehydration with hydroxyl groups. Furthermore, according to the report by Nishikori *et al.*, it has been confirmed that in the complex formed on the TiO_2 surface through the coordination of 2,3-DN involving a dehydration reaction, electron injection occurs from the HOMO of 2,3-DN to the CB of TiO_2 upon light irradiation [50]. In this reaction, a comparable mechanism to these previous studies suggests that the increased visible light absorption of the TiO_2 itself could promote the DBT oxidation (Fig. 15). Based on the experimental results, it is considered that compounds capable of

interacting with the catalyst in this reaction system include toluene, as well as benzyl alcohol, benzaldehyde, and benzoic acid, which can be produced by the oxidation of toluene; and cyclohexanol and cyclohexanone, which can be produced by the oxidation of cyclohexane. Between toluene or toluene-derived compounds and titanium oxide, OH- π interactions could occur between the π electrons of the aromatic ring and the hydroxyl groups on the titanium oxide surface. In addition, in benzyl alcohol and benzoic acid, complex formation may proceed via dehydration between the terminal hydroxyl groups and the hydroxyl groups on the catalyst surface. Furthermore, since this reaction occurs in an oxidative atmosphere, cyclohexanol and cyclohexanone were likely to be oxidized, producing phenol-like derivatives, which were also thought to contribute to activation through OH- π interactions and dehydration-type complex formation. As a result, it was thought that the combined effects of increased visible light absorption of the catalyst due to interactions and enhanced charge transfer associated with complex formation contribute to improved catalytic activity. Subsequently, the electrons were excited to the CB of TiO₂ by the irradiated visible light, and holes (h^+) were generated on the VB. In the CB, excited electrons reacted with oxygen to form $\cdot O_2^-$. In the VB, water or organic compound-derived R-OOH species reacted with h^+ to form $\cdot OH$. In addition, DBT adsorbed on the catalyst surface reacts with h^+ to convert into DBT cation. The cations generated in this step reacted with dissolved oxygen or oxygen radicals formed on the catalyst, undergoing oxidation via an intermediate thought to be DBTO to form DBTO₂.

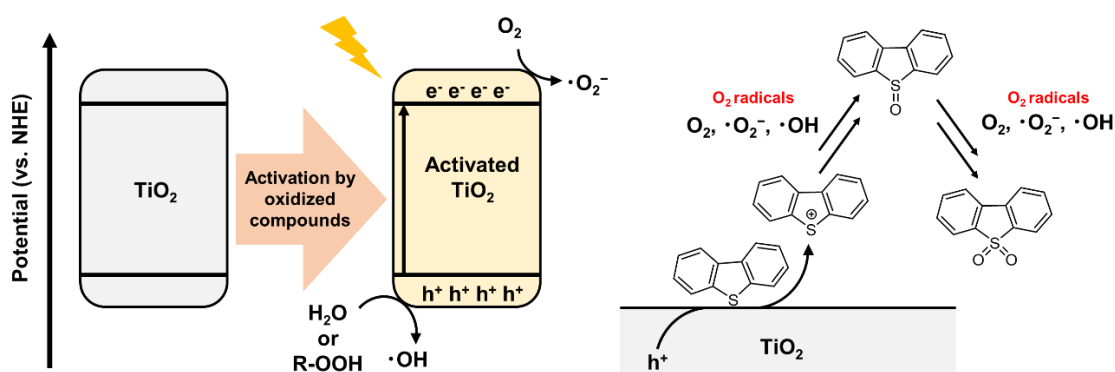


Fig. 14. Possible mechanism of DBT photo-oxidation

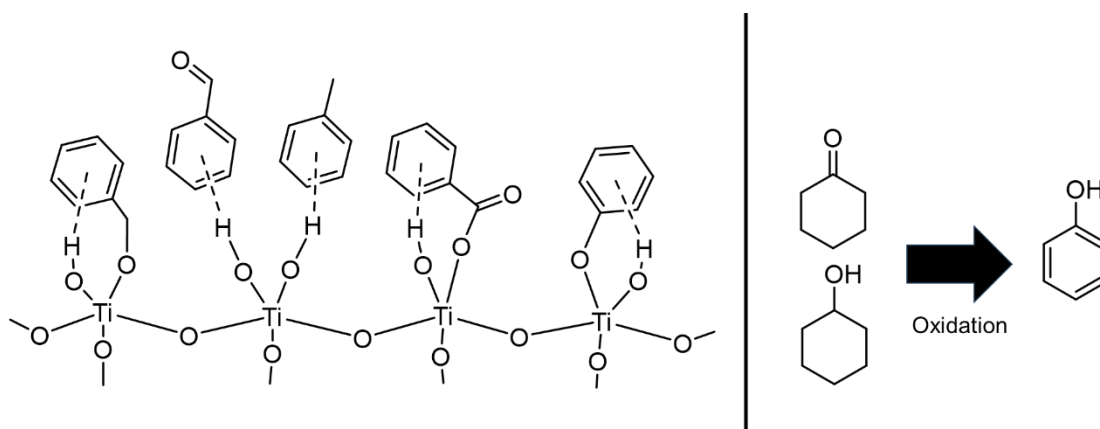


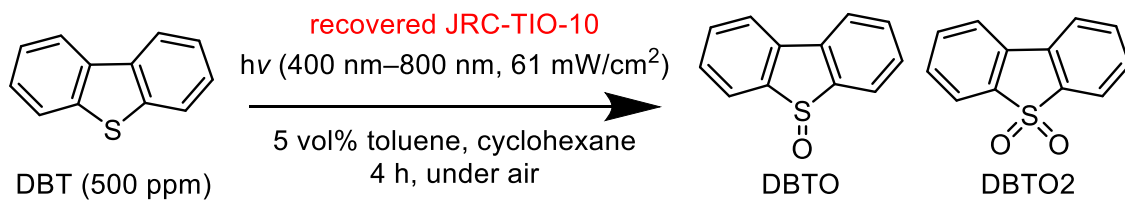
Fig. 15. Possible mechanism of catalyst activation by organic compounds in fuel

2.4. Study of catalyst reusability

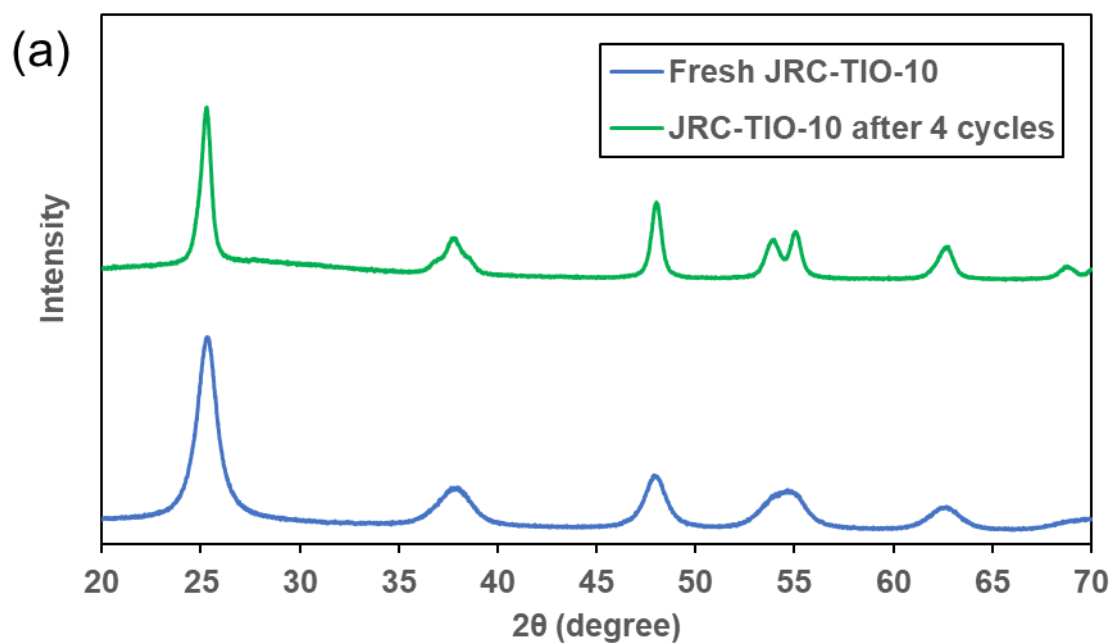
The reusability of the catalyst in this reaction was evaluated. Using JRC-TIO-10 as the catalyst, evaluation was performed via 4 h photo-oxidation using a model fuel (DBT 500 ppm). After each reaction, the recovered catalyst was calcined at 500°C for 1 h and used in the next experiment. Table 7 shows the results after up to four cycles. The DBTO₂ yield decreased to 41% in the first cycle (entry 2), confirming a decrease in activity with repeated reuse. The XRD of the catalyst after four cycles was measured (Fig. 16 (a)). The broad diffraction peak observed at $2\theta = 54.6^\circ$ in the pre-reaction catalyst XRD separated

into two peaks at $2\theta = 53.9^\circ$ and 55.0° , corresponding to the (105) and (211) planes of anatase TiO_2 , respectively. A peak corresponding to the (116) plane of anatase TiO_2 appeared at $2\theta = 68.8^\circ$ [46]. The clear observation of these peaks indicates improved crystallinity of the catalyst after four regeneration cycles. To investigate the cause of this structural change, characterization was performed on JRC-TIO-10, which had only undergone calcination at 500°C . XRD measurements revealed peak separation and peak appearance similar to those observed in the catalyst after four reuses (Fig. 16 (b)). Furthermore, measurement of the specific surface area of this catalyst confirmed a reduction to $99 \text{ m}^2/\text{g}$, compared to $243 \text{ m}^2/\text{g}$ before calcination. These results indicate that the structural changes in the catalyst or the decrease in specific surface area due to the pre-reuse calcination treatment are factors contributing to the decrease in activity in this reuse study. These results suggested that further investigation of the calcination temperature before reuse is necessary, and that maintaining a highly active catalyst state may be possible through optimization of the calcination temperature. Furthermore, the FT-IR spectra shown in Fig. 16 (c) showed only a slight peak detected at 1635 cm^{-1} corresponding to the Ti-OH stretching vibration and almost no change compared to the fresh catalyst, indicating no change in the surface state [47].

Table 7. Study of catalyst reusability



Entry	Cycle	Conv. (%)	DBTO (%)	DBTO2 (%)
1	0	95	0	76
2	1	58	0	41
3	2	35	0	33
4	3	25	0	8
5	4	19	1>	7



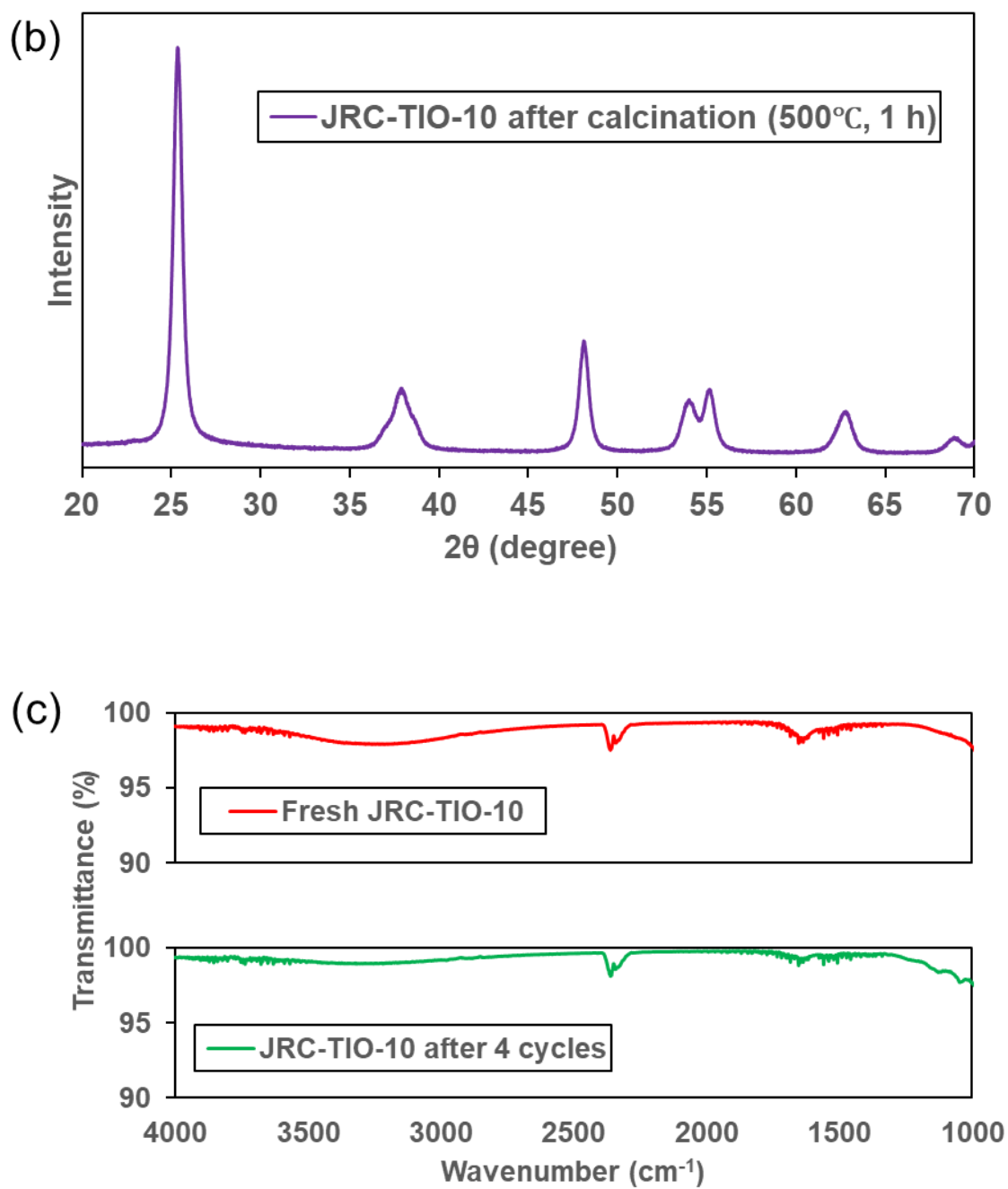
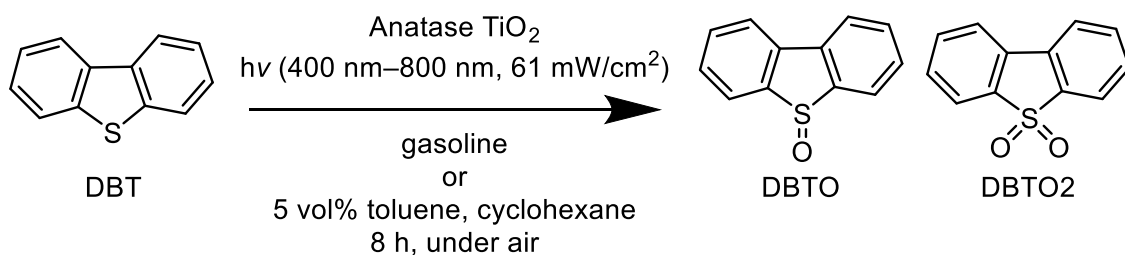


Fig. 16. (a) XRD patterns of JRC-TiO-10 after 4 cycles. (b) XRD pattern of JRC-TiO-10 calcined at 500°C for 1 h. (c) FT-IR spectra of JRC-TiO-10 after 4 cycles.

2.5. Study intended for practical use

The author performed evaluations under more stringent conditions, anticipating the practical application of this reaction system. For the experiments, the author used model fuel containing DBT (1000 ppm) as a sample with high concentration sulfur compounds and commercially available gasoline with DBT (500 ppm) added. Then, using anatase-phase TiO_2 as the catalyst, the author investigated the 8 h photo-oxidation. In the case of high-concentrated model fuel (DBT 1000 ppm), the DBT conversion exceeded 90%, with yields of 76% and 63% (Table 8, entries 1 and 2). On the other hand, using gasoline (DBT 500 ppm) resulted in moderate conversion and yield (entries 3 and 4). These results demonstrated that this TiO_2 -catalyzed photo-oxidation was an excellent method applicable even under practically relevant conditions.

Table 8. Study for the application (8 h reactions)

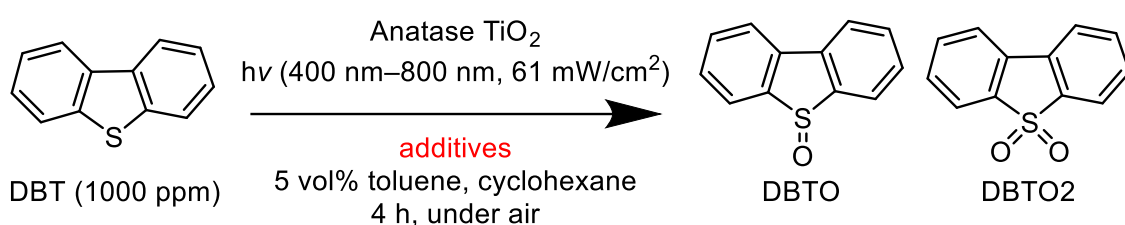


Entry	Sample	DBT (ppm)	TiO_2	Conv. (%)	DBTO (%)	DBTO2 (%)
1	Model fuel	1000	ST-01	97	0	76
2	Model fuel	1000	JRC-TIO-10	94	1	63
3	Gasoline	500	ST-01	44	0	43
4	Gasoline	500	JRC-TIO-10	57	0	43

To explore more efficient reaction conditions, the author investigated the effects of additives in this reaction. The verification of additive effects was conducted using a 4 h reaction with JRC-TIO-10 and a cyclohexane solution containing DBT (1000 ppm). The results are shown in Table 9. First, without additives, the DBTO₂ yield after a 4 h reaction was 13% (entry 1). When 0.6 eq of benzaldehyde was added relative to the amount of DBT (mole), the yield increased to 29% (entry 2). Furthermore, when examining 2,3-DN and 1-naphthol (1-NAP) previously studied in prior research, the addition of 1-naphthol increased the DBTO₂ yield to 47% (entry 3). Additionally, when considering the addition of dithranol as an analog of these additives, DBT conversion was 74%, and the DBTO₂ yield was 50% (entries 4 and 5). Based on these results, dithranol was determined to be the optimal additive. Further investigation revealed that replacing the catalyst with ST-01 yielded superior results compared to using JRC-TIO-10 (entry 6). Also, when the additive amount was set to 1 eq relative to DBT (mole), the DBTO₂ yield increased to 72% (entry 7). Catalyst-free conditions were also examined; however, the reaction did not proceed, and it was determined that dithranol itself does not function as a photocatalyst (entry 8). Based on this result, it was considered that dithranol enhances catalytic activity by acting on titanium dioxide within the system. Specifically, referring to the research by Kamegawa *et al.*, it was thought that the three hydroxyl groups of dithranol bind to the hydroxyl groups on the catalyst surface via a dehydration mechanism, forming a complex and consequently improving catalytic activity [49] (Fig. 17). Furthermore, since dithranol possessed more hydroxyl groups than 1-NAP or 2,3-DN, it was presumed that dithranol's greater propensity for interaction and its more robust binding was responsible for the difference in catalytic performance. In a system containing 1 eq of dithranol, the reaction in gasoline was also investigated. As shown in Table 10, when dithranol was not added,

the DBT conversion rate was 57%, and the DBTO2 yield was 41% after a 4 h reaction (entry 1). With the addition of dithranol, both anatase-phase titania catalysts achieved high conversion in a 4h reaction, with ST-01 achieving over 80% DBTO2 yield (entries 2 and 3). These results suggest that promoting visible light absorption in the catalyst using appropriate additives could lead to the development of even higher-activity catalysts.

Table 9. Study for application using additives (DBT 1000 ppm model fuel, 4 h reaction)



Entry	TiO ₂	Additives	Amount (eq)	Conv. (%)	DBTO (%)	DBTO2 (%)
1	JRC-TIO-10	—	—	44	1	13
2	JRC-TIO-10	Benzaldehyde	0.6	53	5	29
3	JRC-TIO-10	2,3-DN	0.5	44	0	20
4	JRC-TIO-10	1-NAP	0.6	68	1	47
5	JRC-TIO-10	Dithranol	0.5	74	0	50
6	ST-01	Dithranol	0.5	>99	0	68
7	JRC-TIO-10	Dithranol	1	87	1>	72
8	—	Dithranol	1	4	0	1>

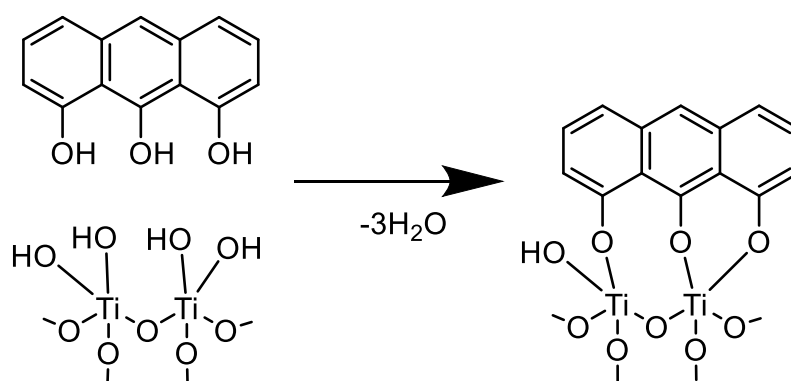
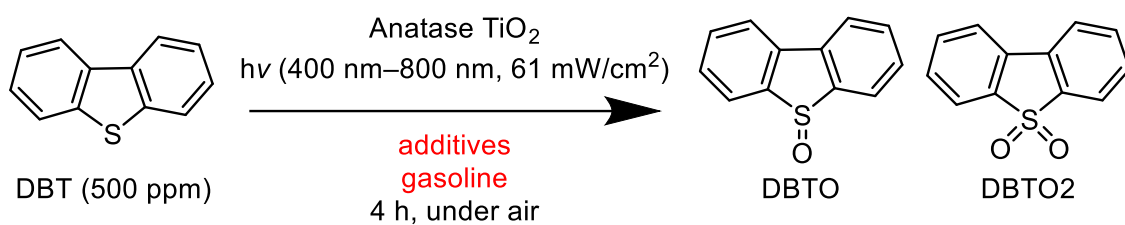


Fig. 17. Possible mechanism of dithranol modification

Table 10. Study for application using additives (DBT 500 ppm gasoline, 4 h reaction)



Entry	TiO ₂	Additives	Amount (eq)	Conv. (%)	DBTO (%)	DBTO2 (%)
1	JRC-TIO-10	—	—	57	0	41
2	ST-01	Dithranol	1	83	0	81
3	JRC-TIO-10	Dithranol	1	80	0	62

3. Conclusion

This study investigated the visible-light oxidation reaction of DBT using TiO_2 , aiming to develop a mild desulfurization method that does not require excess oxidant. Using model fuels, it was found that the anatase-phase TiO_2 is suitable for this reaction. Specifically, when the reaction rates of anatase-phase and rutile-phase catalysts during the initial reaction stage were determined from pseudo-first-order plots, it was found that the anatase-phase catalyst was approximately 3.2 times larger. Detailed investigation and analysis also suggested that organic compounds originating from toluene or solvents in the model fuel influence catalytic activity. In addition, this reaction was confirmed to proceed under visible light irradiation alone, with an external quantum yield of 1.5×10^{-1} when using an LED ($\lambda = 430 \text{ nm}$, 80 mW). Furthermore, experiments using radical scavengers yielded results suggesting that oxygen radicals were generated during the reaction. Therefore, this photo-oxidation is thought to proceed through initial catalyst activation, followed by electron excitation and oxygen radical generation, leading to DBT oxidation. Also, when considering catalyst reusability, activity decreased to approximately half its initial level after the first reuse. The author hypothesized that the treatment temperature of the catalyst before reuse is the cause of this deactivation, and temperature optimization remains a future challenge. Furthermore, moderate to high activity was achieved even in model fuels containing high concentrations of DBT and in DBT-added gasoline. Then, the addition of dithranol as a reaction-promoting additive enhanced the catalytic activity, achieving an 81% DBTO₂ yield after a 4h photo-oxidation in gasoline. This system is suitable for the desulfurization of liquid fuels under mild

conditions without requiring additional oxidants. The results of this study suggest that the photo-oxidation system using a TiO_2 catalyst is a practical method.

Experimental section

1. Materials

Benzaldehyde ($\geq 98\%$), benzyl alcohol ($\geq 99\%$), cyclohexanol, DBT ($\geq 98\%$), dichloromethane ($\geq 99.5\%$), 1-NAP ($\geq 99\%$), and toluene ($\geq 99.5\%$) were purchased from Wako Pure Chemical Industries, Ltd. 1,4-BQ ($\geq 98\%$), 3-chloroperoxybenzoic acid (*m*-CPBA) ($\geq 65\%$), cyclohexane ($\geq 99.5\%$), cyclohexanone ($\geq 99\%$), DBTO2 ($\geq 98\%$), DBSF ($\geq 98\%$), DBSFO ($\geq 96\%$), 2,3-DN ($\geq 98\%$), and dithranol ($\geq 95\%$) were purchased from Tokyo Chemical Industry Co., Ltd. DBSFO2 ($\geq 99\%$) was purchased from Sigma-Aldrich. DMSO ($\geq 99\%$) was purchased from Kishida Chemical Co., Ltd. Regular gasoline was purchased from ENEOS Corporation. Various types of TiO₂, including ST-01 (Ishihara Sangyo Kaisha, Ltd., $\geq 93\%$, particle size: 7 nm, BET surface area (S_{BET}) = 250 m²/g), JRC-TIO-10 (reference catalyst, The Catalysis Society of Japan, particle size: 15 nm, S_{BET} = 243 m²/g), P-25 (EVONIK Japan Co., Ltd., $\geq 99\%$, particle size: 21 nm, S_{BET} = 46 m²/g), and STR-100N (Sakai Chemical Industry Co., Ltd., $\geq 95\%$, particle size: 15 nm, S_{BET} = 77 m²/g), were used.

2. Experimental procedures

2.1. General procedures of DBT photo-oxidation

Model fuels (DBT 500 ppm, 2.7 mmol/L and DBT 1000 ppm, 5.4 mmol/L) were synthesized by dissolving DBT in cyclohexane containing 5 vol% toluene. Model fuels (DBSF 500 ppm, 3.4 mmol/L) were synthesized by dissolving DBSF in cyclohexane containing 5 vol% toluene. DBT-added gasoline (500 ppm) was synthesized by dissolving DBT in regular gasoline. Before photo-oxidation, TiO₂ (87.8 mg) was placed in a quartz tube and annealed at 100 °C for 1 h (heating rate: 10 °C/min) using an electric furnace. After cooling to room temperature, 3 mL of the model fuel was added to the quartz tube with a screw cap. Visible light irradiation was performed for 4 h using a halogen lamp (Schott Megalight100, 100 W, $\lambda = 400\text{ nm}–800\text{ nm}$, 120000 lx, 61 mW/cm²). The reaction mixture supernatant was removed by centrifugation and decantation. Then, ethanol (3.0 mL) was added to the quartz tube and stirred for 24 h to extract the reaction products. The reaction mixture and extract were analyzed using gas chromatography (SHIMADZU GC-2010 Plus equipped with an Agilent J&W HP-1 column) and a mass spectrometer (SHIMADZU GCMS-QP2010 SE) to estimate the conversion and yield. The conversion and yield were estimated using the absolute calibration method and Equations (1) and (2). The conversion and yield shown in the article are the total values obtained by analyzing the reaction mixture and the extract. Detailed analysis results are shown in the Appendix section.

$$\text{Conversion (\%)} = \left(1 - \frac{\text{DBT in reaction mixture (mol)} + \text{DBT in extract (mol)}}{\text{initial amount of DBT (mol)}}\right) \times 100 \quad (1)$$

$$Yield (\%) = \frac{DBTO, DBTO_2 \text{ in reaction mixture (mol)} + DBTO, DBTO_2 \text{ in extract (mol)}}{\text{initial amount of DBT (mol)}} \times 100 \quad (2)$$

2.2. Estimation of reaction rates using pseudo-first-order plots

Model fuels (DBT 500 ppm, 2.7 mmol/L) were synthesized by dissolving DBT in cyclohexane containing 5 vol% toluene. The catalysts used were anatase-phase JRC-TIO-10 and rutile-phase STR-100N. Visible light irradiation was performed for 0.5, 1, and 2 h using a halogen lamp (Schott Megalight100, 100 W, $\lambda = 400 \text{ nm} - 800 \text{ nm}$, 120000 lx, 61 mW/cm²). The concentration profile of DBT during the initial reaction stage was plotted using a pseudo-first-order kinetic equation (equation (3)), and the apparent rate constant (k_{app}) was derived. C_0 , C , and t were the initial concentration of DBT, concentration of DBT after reaction, and reaction time (min). Furthermore, the DBT concentration used to calculate the k_{app} is the average value obtained by measuring each sample three times at each reaction time. Other experimental conditions and analytical methods are equivalent to the general procedures.

$$-\ln\left(\frac{C}{C_0}\right) = k_{app}t \quad : (3)$$

2.3. DBT photo-oxidation using a white LED with a long-pass filter

Model fuels (DBT 500 ppm, 2.7 mmol/L) were synthesized by dissolving DBT in cyclohexane containing 5 vol% toluene and without it. Model fuels using hexane as the solvent were prepared by the same method. Visible light irradiation was performed for 4

h using a white LED (Asahi Spectra, 3 W, $\lambda = 400\text{ nm}–800\text{ nm}$, 120000 lx, 43 mW/cm²) with a long-pass filter (Asahi Spectra, $\lambda > 422\text{ nm}$). Other experimental conditions and analytical methods are equivalent to the general procedures.

2.4. External quantum yield estimation

First, JRC-TIO-10 (87.8 mg) was placed in a capped four-sided quartz cell and heat-dried at 101 °C for 1 h. Next, the model fuel (5 vol% toluene-cyclohexane solution containing 500 ppm DBT, 3 mL) was added, and visible light irradiation was performed under stirring. Monochromic LED lamps ($\lambda = 430, 455, 470,$ and 505 nm , THOLABO, Japan) were used as the light source. The light intensity of all LEDs was adjusted to 80 mW. The amount of DBT reacted was quantified from the absorbance at 326 nm in the UV-vis absorption spectrum of the reaction solution. Spectra were measured using a SHIMADZU UV-2600 spectrophotometer equipped with a quartz cell. The measurement background used cyclohexane containing 5% toluene. The measurement samples used reaction solutions irradiated with visible light for 1, 2, 5, 10, 20, 30, 45, and 60 minutes. Each sample was dispensed into 15 μL aliquots, diluted 200-fold, and then used for spectroscopic measurements. The external quantum yield (ϕ_{ex}) was calculated based on the amount of reacted DBT and the number of incident photons using Equation (4):

$$\phi_{ex} = \frac{\text{Number of reacted DBT molecules}}{\text{Number of irradiated photons}} \quad (4)$$

2.5. Preparation of irradiated TiO₂ samples

JRC-TIO-10 (87.8 mg) was placed in a capped quartz tube and annealed at 100 °C for 1 h (heating rate: 10 °C/min) using an electric furnace. After that, toluene or cyclohexane (3 mL) was added to the tube and irradiated for 1 h (Schott Megalight100, 100 W, $\lambda = 400\text{ nm}–800\text{ nm}$, 120000 lux, 61 mW/cm²). After exposing JRC-TIO-10 to visible light in these solvents, the samples were dried at 110 °C for 1 h.

2.6. Evaluation of catalyst reusability

Model fuels (DBT 500 ppm, 2.7 mmol/L) were synthesized by dissolving DBT in cyclohexane containing 5 vol% toluene. The catalyst used was JRC-TIO-10. Visible light irradiation was performed for 4 h using a halogen lamp (Schott Megalight100, 100 W, $\lambda = 400\text{ nm}–800\text{ nm}$, 120000 lx, 61 mW/cm²). After photo-oxidation, the recovered catalyst was calcined at 500°C for 1 h and used in the next experiment.

2.7. DBTO synthesis

DBTO was synthesized according to a previously reported method [51]. To a solution of DBT (0.74 g, 4.0 mmol) in dichloromethane (14 mL) in a 200 mL eggplant flask, m-CPBA (0.69 g, 4.0 mmol) was slowly added at 0 °C. The mixture was stirred at 0 °C for 4 h. The mixture was then gradually heated to room temperature and stirred overnight. Subsequently, the reaction was quenched with saturated NaHCO₃ aqueous solution. The aqueous layer was then extracted using dichloromethane (3 × 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under vacuum. The obtained residue was purified using column chromatography on silica gel to obtain DBTO.

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 7.6$ Hz, 2H), 7.81 (d, $J = 7.7$ Hz, 2H), 7.62 – 7.57 (m, 2H), 7.52 – 7.47 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 137.1, 132.5, 129.5, 127.5, 121.9.

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer at 400 and 100 MHz, respectively. The ^1H assignment abbreviations are: doublet (d) and multiplet (m).

3. Characterization methods

3.1. X-ray diffraction (XRD) analyses

XRD analyses were performed using a Rigaku MiniFlex 600 diffractometer with high-intensity $\text{Cu K}\alpha$ radiation ($\lambda = 0.151478$ nm). The operating voltage and current were set to 40 kV and 15 mA, respectively.

3.2. UV-vis diffuse reflectance spectra measurements

UV-vis spectra of the catalyst were obtained by the diffuse reflectance method using a JASCO V-670 spectrophotometer, with Spectralon® (Labsphere) employed as the reflectance standard. The bandgap energy (E_g) of the catalyst was determined from a Tauc plot generated by converting the UV-vis spectrum measured using equation (5). $F(R_\infty)$ is a constant obtained from the Kubelka-Munk equation (equation (6)) using the reflectance (R_∞) of the catalyst. Here, h , ν , and A are Planck's constant, the frequency of light, and a constant, respectively. After plotting $(F(R_\infty)h\nu)^{0.5}$ as a function of energy ($h\nu$), the bandgap

energy was estimated by extrapolating the linear region of the plot to intersect the energy axis.

$$(F(R_{\infty})h\nu)^{0.5} = A(h\nu - E_g) \quad (5)$$

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}}. \quad (6)$$

The VB energy (E_{VB}) and CB energy (E_{CB}) of the catalyst were calculated using equations (7) and (8), respectively. Here, X is the absolute electronegativity of TiO_2 (5.81 eV), and E_0 is the energy of a free electron in the hydrogen scale (4.5 eV).

$$E_{CB} = X - E_0 - 0.5E_g \quad (7)$$

$$E_{VB} = E_{CB} + E_g. \quad (8)$$

3.3. Fourier transform infrared (FT-IR) spectra measurements

The FT-IR spectra of the catalysts were measured using attenuated total reflection (ATR). FT-IR spectra were obtained using a JASCO FT/IR-6100 and ATR PRO450-S with a resolution of 2.0 cm^{-1} .

Appendix

They are detailed results of the gas chromatography analyses conducted using a mass spectrometer.

Table A1. detailed analysis results (in Table 1)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	1>	0	0
	Extract	17	4	70
2	Reaction mixture	1	0	1
	Extract	1>	0	67
3	Reaction mixture	3	0	0
	Extract	1>	0	78
4	Reaction mixture	1>	0	2
	Extract	5	0	74
5	Reaction mixture	0	0	0
	Extract	3	0	84
6	Reaction mixture	1>	0	0
	Extract	1	0	92
7	Reaction mixture	40	0	1>
	Extract	26	0	16

8	Reaction mixture	62	0	1>
	Extract	16	1	5
9	Reaction mixture	75	0	0
	Extract	N/D	N/D	N/D
10	Reaction mixture	67	0	0
	Extract	18	0	1

Table A2. Detailed analysis results (in Table 2)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	2	0	0
	Extract	24	6	53
2	Reaction mixture	1>	0	2
	Extract	5	0	74
3	Reaction mixture	1>	0	0
	Extract	6	0	86
4	Reaction mixture	1>	0	0
	Extract	8	0	58
5	Reaction mixture	1>	0	0
	Extract	1	0	99

6	Reaction mixture	1>	0	0
	Extract	1	0	>99
7	Reaction mixture	1	0	0
	Extract	14	0	74
8	Reaction mixture	2	0	0
	Extract	13	0	62

Table A3. Detailed analysis results (in Table 4)

Entry	Solution	Remained DBSF (%)	DBSFO (%)	DBSFO2 (%)
1	Reaction mixture	4	0	1>
	Extract	2	30	72
23	Reaction mixture	>99	0	0
	Extract	1>	0	0
3	Reaction mixture	95	0	0
	Extract	N/D	N/D	N/D

Table A4. Detailed analysis results (in Table 5)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	9	0	0
	Extract	45	1	10
2	Reaction mixture	10	0	0
	Extract	33	0	17
3	Reaction mixture	27	0	0
	Extract	31	0	2
4	Reaction mixture	6	0	0
	Extract	44	0	20

Table A5. Detailed analysis results (in Table 6)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	0	0	0
	Extract	25	0	53
2	Reaction mixture	23	0	0
	Extract	33	1	17
3	Reaction mixture	10	0	0
	Extract	54	8	14

4	Reaction mixture	2	0	0
	Extract	50	6	34
5	Reaction mixture	52	0	0
	Extract	34	3	6
6	Reaction mixture	59	0	0
	Extract	27	0	3

Table A6. Detailed analysis results (in Table 7)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	1>	0	2
	Extract	5	0	74
2	Reaction mixture	2	0	7
	Extract	41	0	35
3	Reaction mixture	12	0	10
	Extract	53	0	24
4	Reaction mixture	38	0	0
	Extract	37	0	8
5	Reaction mixture	44	0	0
	Extract	38	1>	7

Table A7. Detailed analysis results (in Table 8)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	1>	0	1>
	Extract	3	0	76
2	Reaction mixture	1	0	3
	Extract	5	1	60
3	Reaction mixture	52	0	15
	Extract	4	0	28
4	Reaction mixture	39	0	14
	Extract	4	0	28

Table A8. Detailed analysis results (in Table 9)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	26	0	0
	Extract	30	1	13
2	Reaction mixture	21	0	0
	Extract	26	5	29
3	Reaction mixture	27	0	0
	Extract	29	0	20

4	Reaction mixture	14	0	0
	Extract	18	1	47
5	Reaction mixture	5	0	0
	Extract	21	0	50
6	Reaction mixture	0	0	4
	Extract	1>	0	68
7	Reaction mixture	1	0	1
	Extract	12	1>	70
8	Reaction mixture	96	0	1>
	Extract	N/D	N/D	N/D

Table A9. Detailed analysis results (in Table 10)

Entry	Solution	Remained DBT (%)	DBTO (%)	DBTO2 (%)
1	Reaction mixture	37	0	17
	Extract	6	0	24
2	Reaction mixture	15	0	36
	Extract	2	0	45
3	Reaction mixture	17	0	25
	Extract	3	0	37

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Acknowledgment

I would like to express my heartfelt gratitude to everyone who supported me in completing this thesis.

I would especially like to express my deep appreciation to my supervisors, Prof. Makoto Tokunaga, Prof. Haruno Murayama, Associate Prof. Eiji Yamamoto, Assistant Prof. Akina Yoshizawa, and Assistant Prof. Akihiro Nakayama, for their invaluable support and insightful advice, which enabled my research to progress smoothly.

I also extend my thanks to all members of the Tokunaga Lab for making my research life meaningful.

I would like to express my gratitude to Prof. Shinsuke Takagi and Assistant Prof. Tetsuya Shimada for their cooperation in the external quantum yield measurement experiments. I would like to express my appreciation to Associate Prof. Hironobu Ozawa for his cooperation in the light intensity measurement.

Finally, special thanks are given to my family and friends for their warm encouragement and support.

This work was supported by JST SPRING, Grant Number JPMJSP2136.

This work was supported by “Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Proposal Numbers JPMXP1224KU1030, and JPMXP1225KU1026.