

Preparation of Titanium Oxide-Fibrous Zeolite Y Catalyst for Desulfurization of Fuel

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ABSTRACT – In this study, TiO₂ supported on fibrous Zeolite Y (FY) was synthesized via ultrasonic co-impregnation for desulfurization of dibenzothiophene (DBT). The physicochemical properties of the prepared TiO₂/FY were characterized by XRD and TEM. Next, to determine the efficiency capacity of TiO₂/FY in the fuel desulfurization process, several photocatalytic tests with different parameters including time (0 – 180 min), TiO₂/FY dosage (0.1 - 5 g/L), initial pH (2 - 8), and initial concentration (50 – 400 mg/L) were conducted accordingly. A high DBT removal (87%) was successfully accomplished at the optimum conditions of 5 g/L TiO₂/FY, pH 8, and 300 mg/L, which may be contributed from the fibrous structure as recorded by TEM and high crystallinity from the XRD analysis. It can be concluded that the TiO₂/FY own great potential to be applied as an efficient material for the fuel desulphurization.

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INTRODUCTION

Mercaptans, disulfides, thiophenes, and sulfides are the several classifications of sulfur compounds. The presence of sulfur in fuel is an important environmental issue that needs to be addressed since it can cause the formation of sulfur dioxide that will react with oxygen and water vapor, further generating sulfuric acid that is responsible for acid rain phenomena [1,2]. Besides, the combustion of sulfur compounds into the environment not only causes acid rain but other environmental hazards due to sulfates and airborne particulates generation [3]. Moreover, the high composition of sulfur compounds in fuels is also established to negatively impact the automobile system itself by plummeting the catalytic converter efficiency. Dibenzothiophenes or known as DBT are the utmost predominant sulfur-containing compounds in the diesel fuel fraction. Therefore they are frequently used as the model oil to signify the organic sulfur either in oil or coal.

Consequently, several studies on the fuel desulphurization field primes to the development of various sulfur removal technologies including selective adsorption, oxidative desulfurization (ODS), hydrodesulfurization (HDS), extractive distillation, and biodesulfurization [3]. Unfortunately, these processes demand higher operating costs, temperatures, and pressure which are not preferable. During the past few years, to save energy and reduce costs, photocatalytic desulfurization under UV irradiation in the presence of a photocatalyst is getting attention mainly due to safety, recycling advantages, and minimum energy consumption [4].

In photocatalysis, one of the efficient semiconductors that have been considered is titanium dioxide (TiO₂). Not only cheap, safe, and stable, TiO₂ also displays high durability, does not corrode easily and has high oxidation potential [5]. However, too rapid charge carrier recombination, low interfacial charge-transfer rates, and recycling difficulties were the main drawbacks of using bare TiO₂. Therefore two common strategies have been proposed for elevating its photoactivity [6]. One of them is via incorporating the TiO₂ on porous supports including fiberglass, activated carbon, zeolites, and as the support materials. Among all the supports, microporous crystalline aluminosilicates i.e zeolites, are the most promising solid support based on their reputations being thermally stable and having high selectivity and capacity in transferring electrons to their abundance of active sites [7]. Meanwhile, fibrous silica as the support material can improve the activity and stability of the catalyst [8]. Mesoporous silica with a fibrous shape has a higher surface area than hexagonal or cubic pore structures [9].

Titanium supported with zeolite has currently been explored for its prospective application in photocatalytic reactions [10]. It has been proposed by previous studies that the photophysical properties of titanium encapsulated within the pores of zeolite for the disintegration of different compounds were successfully improved [7]. Meanwhile, the introduction of fibrous silica has been deduced to improve the photocatalytic activity of TiO₂ nanoparticles due to the boosted adsorptive activities and thermal stability from the presence of the mesoporous silica nanosphere [11].

Therefore, by exploiting the attractive features of both of these materials, this study reports on the preparation of TiO₂ supported on fibrous silica Y zeolite for the desulfurization of DBT using a photodegradation approach. The chemical characterization as well as its photodegradation efficiency of DBT are investigated and reported in this work.

METHODOLOGY

Preparation of Fibrous Silica Y Zeolite

Fibrous silica Y zeolite (FY) was synthesized via crystal-seed crystallization using Y zeolite seed (Zeolites, CBV 901, Si/Al: 80). Briefly, one mole of tetraethyl orthosilicate (TEOS, Merck) was mixed with toluene (Merck) and 1-butanol (Merck). The solution was stirred for 30 minutes. Then, the Y zeolite seed was added to the solution followed by stirring for 30 minutes. Then, urea, cetyltrimethylammonium-ammonium bromide (CTAB, Merck), and distilled water solution mixture were added. The consequent combination was agitated and then proceeded to the aging process in a Teflon-sealed microwave reactor at 373 K and 12 hours. The white slurry solution was repeatedly washed, sieved, desiccated at 383 K for 12 hours, and followed by a sintering process at 823 K for 6 hours. The synthesized catalysts are indicated as fibrous silica Y zeolite (FY).

Preparation TiO₂/FY

The TiO₂/FY was generated from the ultrasonic co-impregnation path. A beaker with a pre-calculated amount of TiO₂ precursor solution (approximately 10 wt.%) and as-synthesized FY was placed for 3 hours in an ultrasonication water bath at 353 K. The generated sample was air-dried in an oven overnight at 383 K and then calcined at 823 K for 6 hours. The attained powders were labeled as TiO₂/FY.

Catalyst Characterization

X-ray diffraction (XRD) analysis was accomplished by using Bruker D8 Advance 2018 and the data were taken within the range of 15° to 75° with the step scan 0.02. Transmission Electron Microscopy (TEM) was conducted by using an HT7800 series microscope to observe the morphology of the sample.

Photocatalytic Testing

The evaluation of the photocatalytic reactivity of the synthesized catalyst was done via the desulfurization of dibenzothiophene (DBT). The photocatalytic tests were conducted in a batch reactor that was equipped with a visible lamp. The experiment was performed at three different parameters, including catalyst dosage (0.1 - 5 g), initial pH (2 - 8), and initial concentration (50 - 400 ppm). The samples were taken out for 30-minute intervals and the residual of the DBT was analyzed by UV-Vis spectrometer at 274 nm. The percentage of removal is calculated by using equation (1):

$$\text{Removal of sulphur (\%)} = (S_0 - S_t) / S_0 \times 100 \quad (1)$$

where, S_0 represents the initial concentration of the sulfur compound in dibenzothiophene, and S_t represents the concentration of the sulfur compound after a specific time interval. All conducted experiments were repeated three times and the average reading was taken as the final record.

RESULTS & DISCUSSIONS

Figure 1 shows the TEM image of FY. The fibrous morphology can be seen indicating successful preparation of FY. The particle surface was uneven, which might be advantageous in maximizing the specific surface area of the catalyst and the active sites, as well as improving the catalytic efficiency [12]. It also can be due to all the metal oxides being interconnected which is beneficial for interparticle charge transfer and improves photocatalytic activity [13].

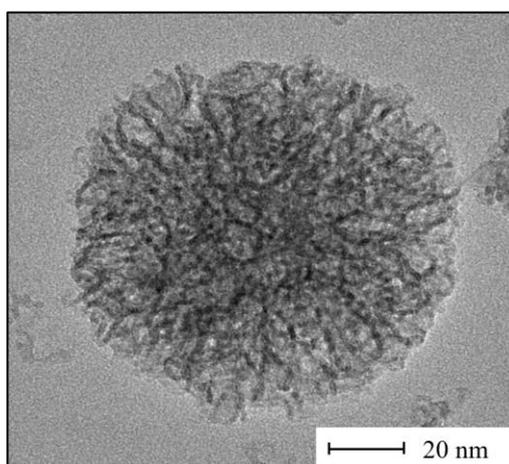


Figure 1. TEM image of FY

Figure 2 illustrates the XRD spectra of FY and TiO₂/FY photocatalyst at the 2θ ranging from 20° to 85°. Five main diffraction peaks were observed for TiO₂/FY at 2θ = 16.21°, 16.23°, 24.30°, 24.34° and 24.36°, which strongly matched with the diffraction planes (1091), (1146), (1082), (1047) and (1066), respectively, as reported in the reference spectral of hexagonal phase TiO₂ (JCPDS No. 01-086-1157). The high crystallinity of TiO₂/FY can benefit in terms of enhancing the photocatalytic activity by delaying e⁻/h⁺ pair recombination and generating additional reactive species for a more efficient reaction between the catalyst and the pollutant [14].

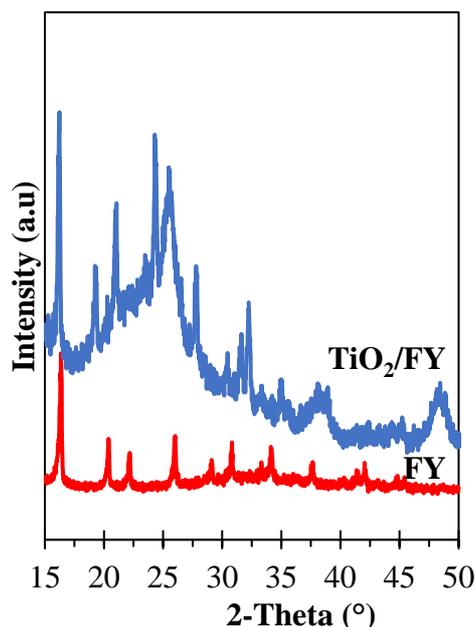


Figure 2. XRD spectra of FY and TiO₂/FY

Figure 3 illustrates the effect of time on the degradation of DBT. As portrayed, at an earlier time stage, prolonging the reaction duration was found to augment the degradation percentage. This scenario might be explained by the higher chance of sulfur interaction with the catalyst active sites at prolonged reaction duration. Nevertheless, at 180 minutes onwards, subsequent time increments then did not greatly impact the sulfur removal process as the equilibrium has been achieved or the surface of the catalyst was already saturated with the DBT [15].

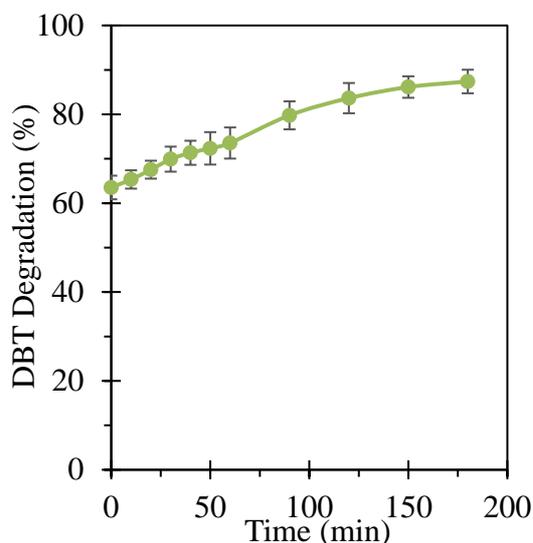


Figure 3. Effect of time on degradation of DBT. Conditions: 5 g/L TiO₂/FY, pH 8, 30 °C, 300 mg/L DBT.

Figure 4 expresses the influence of catalyst dosage on the degradation of DBT. The degradation efficiency showed a significant increase of up to 85% for the dosage of 5 g/L, 55% for 0.1 g/L, 58% for the dosage of 1 g/L, and 59% for 3 g/L. The optimum catalyst dose for the photocatalytic reaction was found to be 5 g/L, by which beyond this amount degradation efficiency was not showing any notable improvement. The elevation of degradation efficiency parallel to the photocatalyst dosage trend may be described by the greater number of available active sites with an increase in photocatalyst dosage. This permitted a higher chance for the contact between the DBT and active sites [16].

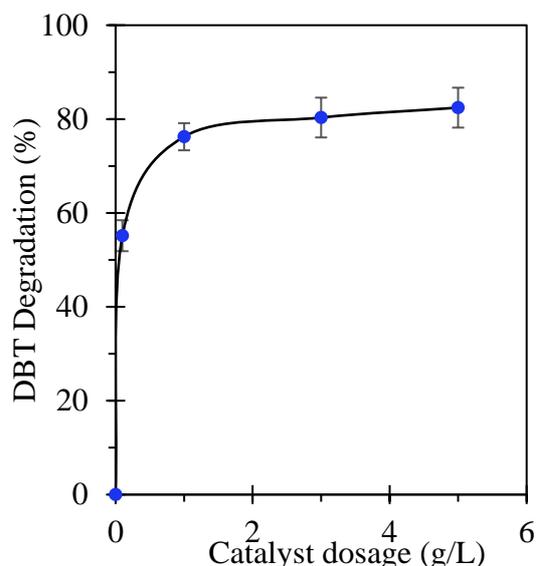


Figure 4. Effect of TiO_2/FY dosage on the degradation of DBT. Conditions: 300 mg/L DBT, pH 8, 30 °C.

As shown in Figure 5, pH exhibited a remarkable impact on the photocatalytic degradation process, as it affected not only the catalyst surface's charge but also the dissociation of the molecule. The results indicated a gradual increase in photocatalytic degradation efficiency (32% to 83%) when the pH environment was modified from pH 2 to pH 8. This might be caused by the reduction of the catalyst's surface positive charges as the pH raises from 2 to 8, which further enhances the attraction of DBT onto the surface of the catalyst. In an alkaline pH environment, the negative site amount in the system also increased which favors the adsorption of DBT cations onto the photocatalyst surface via electrostatic attraction which further caused the DBT removal rate to increase remarkably [17].

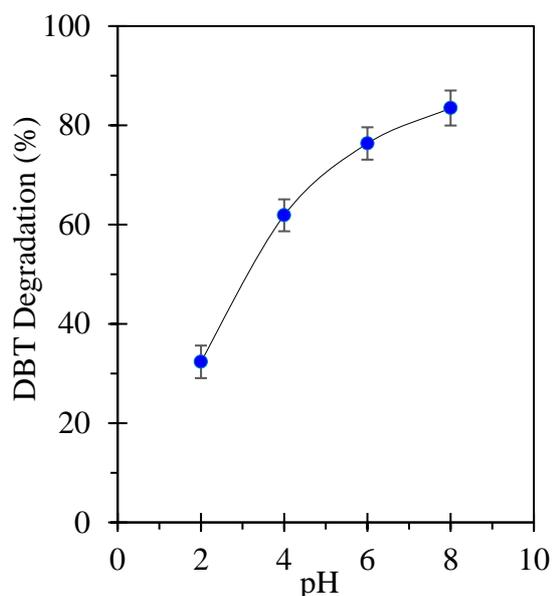


Figure 5. Effect of pH on the degradation of DBT. Conditions: 5 g/L TiO_2/FY , 300 mg/L DBT, 30 °C

Figure 6 illustrates the relation between the initial DBT concentration with the photocatalytic performance. As obtained, there was a significant correlation between the degradation efficiency with the DBT concentration. The rate of photocatalytic degradation increased gradually from 50 to 300 ppm (52% to 87%) but reduced to 70% for 400 ppm. The degradation rate at the most concentrated DBT solution was the lowest as more time was required to reach the equilibrium along with the increase in the amount of unreacted DBT

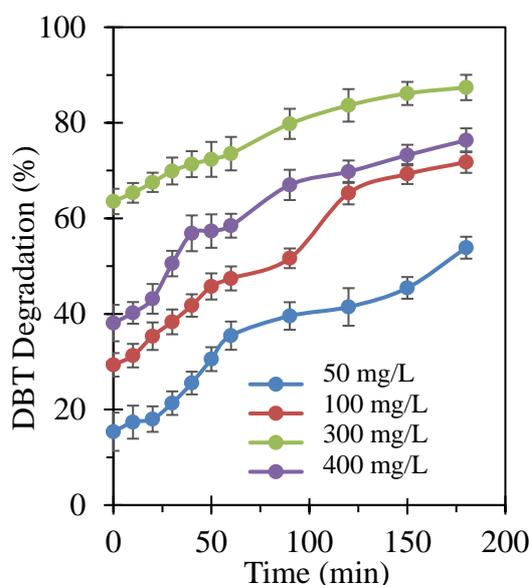


Figure 6. Effect of initial DBT concentration on degradation of DBT. Conditions: 5 g/L TiO₂/FY, pH 8, 30 °C

For comparison purposes, Table 1 summarizes the previous reports of other related zeolite and fibrous silica-supported photocatalyst performances for DBT degradation. As shown, TiO₂-FY generated from this work surpasses the performance of the previously reported catalyst that acquire visible light irradiation such as Cu-fibrous silica (only 62.6%). From the table also, it can be perceived that most of the reported photocatalysts require UV irradiation to achieve respective DBT degradation percentages which are not practical when considering large-scale applications. The synergetic effect between the zeolite and fibrous silica in upgrading the functionality of TiO₂ was proven in this study as, with just visible light irradiation, as much as 87% of the DBT was managed to be degraded. The successful TiO₂ dispersion onto highly fibrous zeolite-FY as indicated by the previous XRD and TEM analysis may benefit in enhancing the photocatalytic capacity during the DBT degradation process.

Table 1. Comparison of DBT photodegradation efficiencies with other related studies

Catalysts	DBT photodegradation efficiencies (%)	Reaction conditions	Refs.
TiO ₂ /Ni-commercial zeolite	99.8%,	UV light, 60°C, catalyst oil/ratio =1.5 mL	[18]
Cu-fibrous silica	62.6%,	100 mg/L initial DBT concentration, visible light, 2 hours, 0.0375 g/L catalyst	[19]
TiO ₂ -zeolite	88%	100 mg/L initial DBT concentration, 10 g/L catalysts, UV source, room temperature,	[20]
TiO ₂ /fibrous zeolite Y (TiO ₂ -FY)	87%	300 mg/L initial DBT concentration, 3 g/L catalysts, pH 8, visible light, room temperature	This work

CONCLUSION

Conclusively, based on the XRD characterization performed, the TiO₂/FY pattern was well-fitted with the HY pattern which specified that the zeolite framework structure was still intact despite the addition of TiO₂. The reactivity of TiO₂/FY in fuel desulfurization was excellent as 87% of DBT degradation was managed to be obtained at the reaction time of 180 minutes, photocatalyst loading of 3 g/L, pH 8, initial DBT concentration of 300 ppm under visible light irradiation. It was believed that the fibrous structure of TiO₂/FY as recorded by TEM and the good crystallinity of the hexagonal TiO₂ from XRD analysis contributed to the outstanding DBT removal result. The results revealed that the TiO₂/FY synthesized from zeolite crystal seed exhibited excellent catalytic activity towards degradation of DBT in visible light irradiation and might be useful for future fuel desulfurization technology.

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