

Photocatalytic Oxidation Kinetics for Desulfurization of Dibenzothiophene with Al₂O₃/g-C₃N₄ Heterojunction

Rui-Hong Liu and Fa-Tang Li*

College of Science, Hebei University of Science and Technology, Shijiazhuang, 050018, China

Abstract: Al₂O₃/g-C₃N₄ heterojunction is fabricated for the photocatalytic removal of dibenzothiophene in oil-water biphasic system and the reaction kinetics is studied. The influences of Al₂O₃/g-C₃N₄ ratio and photocatalyst dosage on reaction rate constant are investigated. The results indicate that the optimum addition of Al₂O₃/g-C₃N₄ composite is 0.075 g in 100 mL reaction system and the photooxidation kinetics of dibenzothiophene follows first-order reaction. The sulfur removal of dibenzothiophene can reach 90.3 % in 4 h under the irradiation of mercury lamp and the sulfur content can be decreased from 200 to below 20 ppm.

Keywords: Desulfurization, Dibenzothiophene, Al₂O₃/g-C₃N₄, Photocatalytic oxidation, Kinetics.

1. INTRODUCTION

Desulfurization from fuel oils has been received much attention because the emitted sulfur oxide (SO_x) caused by the sulfur-containing compounds during the combustion of fuels is a one of the main sources leading to both air pollution and acid rain [1]. In order to protect environment against contamination and minimize the negative effect for human health, most of the countries worldwide have mandated a reduction in the sulfur content in motor fuels. Conventional catalytic hydrodesulfurization (HDS) is taken due to its high efficiency in removing thiols, sulfides, and disulfides [2]. However, it is difficult to desulfurize the dibenzothiophene (DBT) and its derivatives by HDS because of their steric hindrance [3]. Furthermore, HDS is generally performed at high pressure (>5MPa) and high temperature (>520K) by reacting hydrogen with sulfur compounds in the presence of highly active catalysts [4], which are severe operating conditions. Therefore, alternative deep desulfurization techniques, able to remove the sulfur from fuels under moderate conditions and without requirements for hydrogen, are needed to be explored.

Photocatalytic oxidation is an efficient technology to degrade various pollutants, including sulfur-containing compounds in oil, and has attracted extensive interesting because of its potential for utilizing solar energy [5-7]. The development of inexpensive and earth-abundant photocatalysts is a prerequisite for realizing practical application of photocatalysis. Recently, polymeric graphite-like carbon nitride (g-C₃N₄) has received much attention as a thermal,

chemical, and photochemical stable semiconductor [8,9]. To improve the quantum efficiency of g-C₃N₄, our group has constructed Al₂O₃/g-C₃N₄ heterojunctions based on the fact that Al₂O₃ is also a kind of cheap and earth-abundant semiconductor and can accept electrons from g-C₃N₄ [10].

In this research, the photocatalytic kinetics for sulfur removal of DBT over Al₂O₃/g-C₃N₄ is investigated. The influences of initial concentration of DBT and dosage of photocatalyst on reaction rate constants are also studied. The fabrication of inexpensive Al₂O₃/g-C₃N₄ hybrid and its application in desulfurization can provide reference for the production of clean oils.

2. EXPERIMENTAL

2.1. Preparation of Al₂O₃/g-C₃N₄ Heterojunction

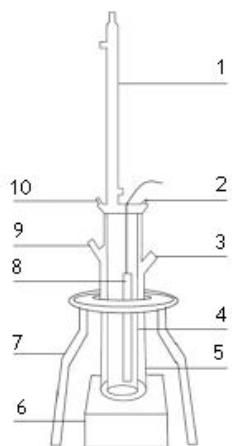
Al₂O₃/g-C₃N₄ composite was prepared by combining surface-hydroxyl-modified g-C₃N₄ and Al₂O₃ obtained *via* combustion synthesis according to Reference [10]. G-C₃N₄ was prepared by heating 5 g of melamine in a covered alumina crucible to 550 °C for 2 h with a heating rate of 10 °C/min. Then 0.1 g of g-C₃N₄ was dispersed into 10 mL of ammonia solution (25wt.%) *via* stirring at room temperature for 5 h. Afterwards, the final powders were collected by centrifugation and dried at 80 °C under vacuum for 4 h. To prepare Al₂O₃, 0.01 mol Al(NO₃)₃·9H₂O was mixed with 0.05 mol of urea and then the mixture was heated in a tube furnace at a heating rate of 10 °C/min and O₂ flow rate of 200 mL/min to 300 °C till the finish of combustion reaction. Then 0.12 g of g-C₃N₄ and 0.08 g of Al₂O₃ were separately added into 50 ml of methanol and sonicated for 30 min. Then these two solutions were mixed and stirred in a covered beaker at room temperature for 24 h. After volatilizing the methanol, Al₂O₃/g-C₃N₄ powders were obtained. The as-synthesized composite is

*Address correspondence to this author at the College of Science, Hebei University of Science and Technology, Shijiazhuang, 050018, China; Tel: +86-311-81669971; Fax: +86-311-81668528; E-mail: lifatang@126.com

denoted as 60%CA, where 60% refers to the g-C₃N₄ weight percents in the composite.

2.2. Photocatalytic Oxidation Desulfurization

The photocatalytic oxidation reaction was conducted in an XPA-II photochemical reactor (Nanjing Xujiang Electromechanical Factory) as shown in Scheme 1. Dibenzothiophene was dissolved in n-octane (50ml) to form model diesel oil with sulfur contents of 200 to 800 ppm. The oil was mixed vigorously with 50mL water and the mixture was UV irradiated by a high-pressure mercury lamp (500W, main wave length 365nm, 0.22kW/m²). Prior photoirradiation, Al₂O₃/g-C₃N₄ and 0.10 g of H₂O₂ solution (30%) were added into the reaction system as photocatalyst and oxidizer. To determine the initial and residual sulfur content, liquid samples were withdrawn from the reactor at fixed time intervals and measured using a ultraviolet fluorescence sulfur analyzer and then desulfurization yield was calculated.



Scheme 1: Schematic diagram of experimental apparatus. 1- condenser tube; 2- inlet of water; 3- inlet of air; 4- silicon cold trap; 5- glass reactor; 6- magnetic stirrer; 7- bracket of reactor; 8- Hg lamp; 9- outlet of air; 10- outlet of water.

3. RESULTS AND DISCUSSION

3.1. XRD Patterns

XRD patterns of g-C₃N₄, Al₂O₃, and Al₂O₃/g-C₃N₄ composite are shown in Figure 1. The diffraction peaks of pure Al₂O₃ are in good agreement with its rhombohedral α -phase (JCPDS No. 081-2267). As for g-C₃N₄, the peaks at 27.4° and 13.2°, corresponding to (002) and (100) planes (JCPDS 87-1526), are due to the stacking of the conjugated aromatic system in graphite and the interlayer structural packing, respectively [11,12], which is consistent with the degrees reported in the literature [12]. With regard to

the Al₂O₃/g-C₃N₄ hybrid, both g-C₃N₄ and Al₂O₃ can be detected, showing its composite structure.

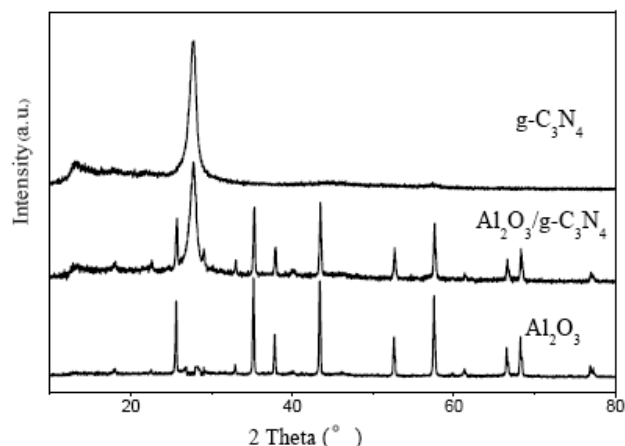


Figure 1: XRD patterns of g-C₃N₄, Al₂O₃, and Al₂O₃/g-C₃N₄ hybrid.

3.2. Influence of DBT Initial Concentration on Photooxidation Kinetics

Figure 2 shows the photocatalytic degradation efficiency of DBT in the presence of H₂O₂ and 0.075 g Al₂O₃/g-C₃N₄ hybrid under the illumination of Hg lamp. Photocatalytic degradation efficiency of DBT is 90.3%, 86.8%, 83.5%, and 80.2% when the initial concentration of DBT is 200, 400, 600 and 800 ppm, respectively.

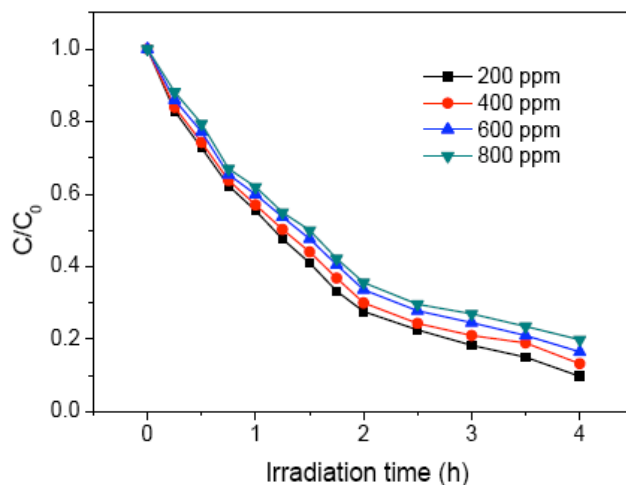


Figure 2: Time-course variation of sulfur removal of dibenzothiophene at different initial concentration (C_0).

The photocatalytic reactions follow the Langmuir–Hinshelwood pseudo-first-order kinetics model when the initial concentration of the reactant is low. The kinetics equation can be expressed as follows [13].

$$\ln C_0/C = kt$$

Table 1: Reaction Rate Constants for Removal of Dibenzothiophene at Different Initial Concentration

Initial Concentration (ppm)	Dynamics Equation	Reaction Rate Constant, k (min^{-1})	Correlation Coefficient (R)
200	$\ln(C_0/C)=0.6213t$	0.6213	0.9951
400	$\ln(C_0/C)=0.5756t$	0.5756	0.9942
600	$\ln(C_0/C)=0.5217t$	0.5217	0.9936
800	$\ln(C_0/C)=0.4931t$	0.4931	0.9935

where k is the pseudo-first-order rate constant, C_0 is the original concentration, C is the concentration at reaction time t .

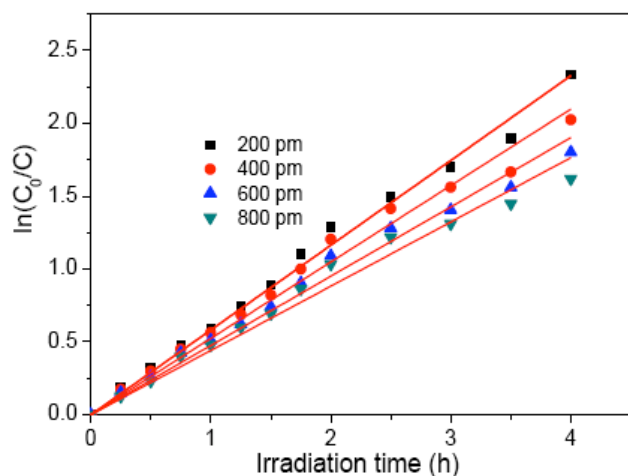


Figure 3: Relationship between $\ln(C_0/C)$ and reaction time of photocatalytic oxidation of dibenzothiophene at initial concentration (C_0) of (a) 200 ppm, (b) 400 ppm, (c) 600 ppm, and (d) 800 ppm.

The time-course variation of $\ln(C_0/C)$ is shown in Figure 3. The corresponding kinetics equations, reaction rate constants, and correlation coefficient are calculated and summarized in Table 1. It is seen that the apparent reaction rate constants increase with decreasing the initial concentration of dibenzothiophene, which is related to the photooxidation products in the water. Dibenzothiophene can be photooxidized to sulfone, SO_4^{2-} , etc, which can be adsorbed on the surface of photocatalyst particles, then poison and reduce the activity of catalyst. The higher the initial concentration is, the more products in the water are. Hence, the higher initial concentration will lead to the adsorption of more product molecules on the surface of $\text{Al}_2\text{O}_3/\text{g-C}_3\text{N}_4$ heterojunction and cause to a lower reaction rate.

3.3. Effect of the Photocatalyst Amount on Disulfurization Yield of Dibenzothiophene

To optimize the reaction condition, the influence of photocatalyst amount on disulfurization yield of

dibenzothiophene was investigated. Figure 4 shows the effect of catalyst amount done by taking 200 ppm DBT model oil for 4 h. When the catalyst amount in 100 mL reaction solution (50 ml oil+50 ml water) is increased from 0.050 g to 0.075 g, then to 0.10 g, the degradation rate of DBT increases from 83.7% to 90.3%, and then slowly to 92.5%, respectively, and the corresponding rate constant is 0.5194, 0.6213, and 0.6449 h^{-1} . This indicates a higher catalyst dosage cause to an elevated reaction rate, because the increase of catalyst amount provides more active sites for DBT, leading to a increase of active species, such as $\cdot\text{OH}$ radical, responsible for the degradation of DBT. However, when excessive catalyst is employed, the reaction rate constant increases slowly due to the scattering of light and reduction in light penetration through the solution [14]. Based on comprehensive consideration of the amount and degradation rate, the 0.075 g in 100 mL reaction solution may be the optimal catalyst dosage.

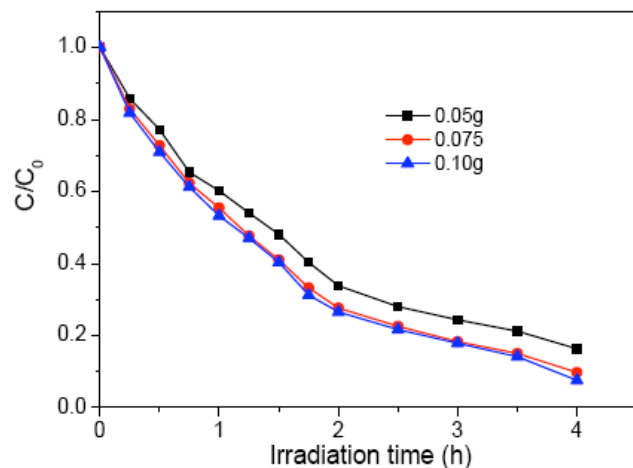


Figure 4: Effect of the photocatalyst amount on disulfurization yield of dibenzothiophene.

4. CONCLUSIONS

The photocatalytic desulfurization process of dibenzothiophene in the presence of $\text{Al}_2\text{O}_3/\text{g-C}_3\text{N}_4$ heterojunction has been investigated. The reaction rate constant increases with the decrease of initial concentration of dibenzothiophene. The optimal

amount of photocatalyst is 0.075 g in 100 mL reaction system. The apparent rate constant is 0.6213 h^{-1} when the initial concentration of dibenzothiophene is 200 ppm and the addition of photocatalyst is 0.075 g. The sulfur content can be depressed from 200 to below 20 ppm in 4 h under ultraviolet light irradiation.

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