



# Oxidative desulfurization of model fuels with pure nano-TiO<sub>2</sub> as catalyst directly without UV irradiation



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## ABSTRACT

In this study, different crystalline forms of nano-TiO<sub>2</sub> were prepared using the sol–gel method. The TiO<sub>2</sub> particles were characterized by X-ray diffraction, transmission electron microscopy, and nitrogen adsorption/desorption measurements. The prepared nano-TiO<sub>2</sub> was directly used as a catalyst to remove dibenzothiophene (DBT) from an octane solution without UV irradiation and with H<sub>2</sub>O<sub>2</sub> aqueous solution as an oxidant. Results showed that anatase TiO<sub>2</sub> nanoparticles have excellent catalytic oxidative activity because conversions as high as 100% were obtained within 50 s under the experimental conditions; by contrast, conversion rates obtained from anatase–rutile and amorphous nanoparticles reached only 48.1% and 25.7%, respectively. The effects of stirring rate, reaction temperature, initial DBT concentration, catalyst amount, and oxidant content were also investigated in detail. Based on the results, a reaction kinetic model implying a first-order reaction with an activation energy of 56 kJ/mol was established. The nano-TiO<sub>2</sub> particles were used to catalyze 4,6-dimethyldibenzothiophene, and the effects of reaction temperature and amount of oxidant used on this reaction were investigated.

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## 1. Introduction

Deep desulfurization of fuel has drawn much attention all over the world because of the air pollution caused by sulfur oxides. Governments around the world have mandated stricter regulations and specifications on sulfur amount in fuel. These strict regulations were recently implemented in many countries for environmental protection, thereby motivating increases in the development of deep desulfurization technologies. Fuel cell applications have also set forth stricter requirements for ultra-deep desulfurization [1,2].

Hydrodesulfurization (HDS) is a traditional method used to remove sulfur compounds but requires high temperatures and pressures to complete. In addition, many sulfur compounds, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), cannot be easily removed through this approach. HDS also requires long residence times to remove the sulfur compounds, making the method extremely difficult to accomplish at the expense of significant decreases in octane number and increases in hydrogen consumption. Thus, HDS can lead to high investment and operating cost [3].

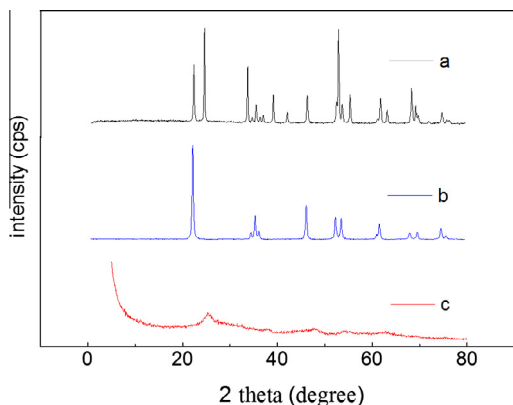
Several new desulfurization technologies, including biodesulfurization [4,5], selective adsorption [6–8], extraction, and oxidative

desulfurization (ODS), have been developed in the past few years [9–14]. Among these methods, ODS is considered one of the most ideal ones because its reaction conditions are quite mild and the reaction may be performed near room temperature and atmospheric pressure [15].

The use of TiO<sub>2</sub> in a number of catalytic applications has been extensively examined because the material presents three main advantages: high specific area, low cost, and feasibility for large-scale production [16]. A number of studies have been conducted on Ti-based materials used as adsorbents in desulfurization [17–20], and these materials are commonly used as photocatalysts. Wang et al. [21] explored the photocatalytic activity of nano-TiO<sub>2</sub> in desulfurization and found that nano-TiO<sub>2</sub> can be prepared in ionic liquids and reduce sulfur contents to 8 and 26 ppm in model oil and actual diesel oil, respectively, after 10 h of UV irradiation. Wang et al. [22] found that TiO<sub>2</sub> located on C<sub>3</sub>N<sub>4</sub>, as a photocatalyst, can achieve DBT conversion rates as high as 98.9% after 2 h. TiO<sub>2</sub> in bamboo charcoal can also enhance this reaction because the catalyst locates at the oil–water phase boundary [23]. The work of Thu et al. [24] showed that MWNTs/TiO<sub>2</sub> as a photocatalyst can remove over 98% of the sulfur in oil because the MWNTs enhance the photocatalysis of TiO<sub>2</sub>. Zhu et al. [25] investigated the effect of TiO<sub>2</sub> forms as photocatalysts in desulfurization and showed that these forms significantly affect the photocatalytic oxidation of TiO<sub>2</sub>. DBT conversion reaches 96.6% in model oil with amorphous TiO<sub>2</sub>

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**Fig. 1.** X-ray powder diffraction patterns of  $\text{TiO}_2$  calcined under different temperatures: (a) 1023 K, (b) 773 K, and (c) 373 K.

but only 23.6% with anatase  $\text{TiO}_2$  and 18.2% with anatase–rutile  $\text{TiO}_2$ .

Several researchers have studied oxidative desulfurization with Ti or  $\text{TiO}_2$  materials [26–28]. Mariana et al. [29] found that  $\text{V}_2\text{O}_5$  located in  $\text{TiO}_2$  as a catalyst exhibits good desulfurization properties. Yan et al. [30] revealed that Lewis acidic sites are very important for removing sulfur oxidants and synthesized  $\text{TiO}_2$  with phosphotungstic acid (HPW) as a catalyst for ODS; results showed that DBT conversion as high as 95.2% may be obtained with increasing  $\text{TiO}_2$ . Huang et al. [31–34] conducted several works on desulfurization with HPW located in  $\text{TiO}_2$ . Arellano et al. [35] explored Fe– $\text{TiO}_2$  as a catalyst in desulfurization and found that 300 ppm of DBT can be removed at pH 0 and 10 wt% Fe by Fe– $\text{TiO}_2$ ; the authors also revealed that Fe and Ti function as active sites in this reaction. Mesoporous TS-1 synthesized through  $\text{SiO}_2$ – $\text{TiO}_2$  can remove 96% of the DBT in oil within 2 h [36].

Although a large amount of research has been devoted to  $\text{TiO}_2$ -materials used as photocatalysts and adsorbents in ODS [37–39], little information on the direct use of pure  $\text{TiO}_2$  as an oxidative catalyst is available. Pure  $\text{TiO}_2$  is easy to produce and recycle, so it is inexpensive. The present aims to study the direct oxidative activity of pure  $\text{TiO}_2$  in deep oxidative desulfurization. Nano- $\text{TiO}_2$  oxidation was tested with  $\text{H}_2\text{O}_2$  as an oxidant to remove DBT from sample oils without UV irradiation. The catalytic activity

of anatase, anatase–rutile, and amorphous  $\text{TiO}_2$  nanoparticles was investigated during DBT removal model fuels. Using anatase  $\text{TiO}_2$  nanoparticles as catalysts, the effects of stirring rate, reaction temperature, initial DBT concentration, catalyst amount, and oxidant content were systematically investigated, and the oxidative desulfurization activities of 4,6-DMDBT on  $\text{TiO}_2$  were explored. Finally, results obtained were compared with those from other similar works.

## 2. Experimental

### 2.1. Materials and chemicals

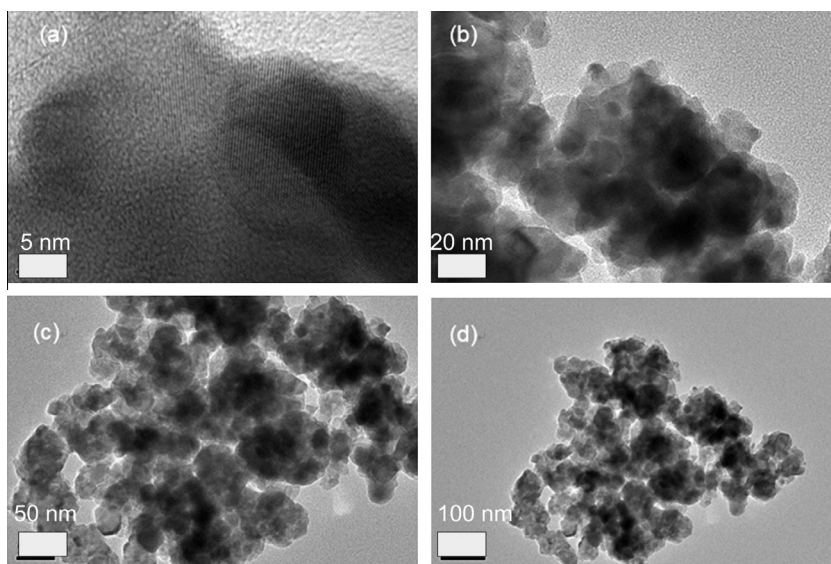
Titanium ethoxide was purchased from Beijing Chemical Plant. Analytical-grade octane was purchased from Fuchen Chemical Plant in Tianjin, China. DBT and 4,6-DMDBT were purchased from Acros Organics. Octadecyltrimethylammonium bromide (STAB) was purchased from Nanjing Robiot Company. All chemicals were used without further purification.

### 2.2. Preparation and characterization of $\text{TiO}_2$ nanoparticles

The  $\text{TiO}_2$  was prepared with STAB as the modifying agent. A total of 7.2 g of titanium ethoxide and 0.05 g of STAB were dissolved in 50.4 g of absolute ethanol under stirring conditions. The resulting suspension was stirred for 3 h at room temperature, and then 10 mL of deionized water was added to it. The solution was stirred for 2 h followed by evaporation in a drying box at 373 K. The obtained solid product was washed thrice with deionized water and then thrice with ethanol. The product was finally dried in a drying box at 373 K for 12 h and then calcined at 773 K for 3 h.

### 2.3. Characterization methods

X-ray diffraction (XRD) patterns of the product were measured with a Rigaku D/max-RB diffractometer in reflection mode using  $\text{Cu K}\alpha$  radiation and voltage of 40 kV. Transmission electron microscopy (TEM) experiments were performed on a JEOL JEM-200CX microscope with at 200 kV operating voltage.  $\text{TiO}_2$  was degassed at 473 K for 200 min as a pretreatment and then measured using a Quantachrome Autosorb-1-C chemisorption-physisorption



**Fig. 2.** TEM images of anatase  $\text{TiO}_2$ .

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