



Full Length Article

Photo-assisted adsorptive desulfurization of hydrocarbon fuels over TiO₂ and Ag/TiO₂

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HIGHLIGHTS

- Ultra-deep removal of organosulfur species by ADS assisted by UV has been developed, without photocatalytic oxidation of sulfur compounds.
- TiO₂/UV system was directly introduced into dynamic sulfur adsorptive process.
- UV during breakthrough experiments increased the sulfur capacity of TiO₂ by 50% under ambient pressure.
- UV along with H₂O enhanced sulfur capacities of TiO₂ and Ag/TiO₂ under ambient conditions.
- Photo-induced active sites (–OH groups) on TiO₂ were observed via *in-situ* IR.

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ABSTRACT

Photo-assisted adsorptive desulfurization (ADS) of hydrocarbon fuels using TiO₂ and Ag/TiO₂ adsorbents under mild conditions has been investigated. UV irradiation ($\lambda = 365$ nm) was directly introduced into the adsorbent packed bed. Typical UV flux at 1 cm from the UV lamp was 1.8–2.0 mW/cm². Sulfur removal performance was evaluated by breakthrough experiments in the presence of UV and H₂O. Results indicated that the sulfur removal capacity of TiO₂ was increased by 50% during UV-assisted ADS. Ag/TiO₂ adsorbents showed the highest UV-assisted capacity which was 6.35 mg S/g adsorbent using a model fuel containing 3500 ppmw sulfur (benzothiophene in *n*-octane) and 1000 ppmw H₂O. *In situ* IR analysis were applied to study the effects of H₂O and UV molecules on surface –OH groups. The chemical state change of Ag caused by UV irradiation was characterized by X-ray Photoelectron Spectrometer (XPS). Based on IR data, the enhanced desulfurization capacity of TiO₂ under UV irradiation was attributed to the increase in the total number of terminal Ti(IV)–OH groups. Multi-cycle experiments will be carried out later to study the stability of UV-activated sulfur removal sites and the photo-assisted sulfur removal mechanism will be investigated in the future.

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1. Introduction

Sulfur compounds are present in nearly all hydrocarbon fuels and represent one of the most common impurities in crude oil, which is a large source of energy. Sulfur and its derivatives in transportation fuels such as gasoline, diesel and jet fuels can be easily converted into SO₂ and fine particles of sulfates during combustion, which are considered as primary pollutants in the air. With the increasing level of sulfur in global supplies of crude oil, desulfurization of fuels has gained great importance due to the demand for clean energy along with environmental concerns [1]. Also, stringent regulations have been applied to limit the maximum sulfur emissions in many countries around the world [2–5].

For example, the allowable sulfur concentrations in the U.S. have been limited to 30 ppmw for gasoline and 15 ppmw for highway diesel since 2006 by Environmental Protection Agency (EPA) regulations [6]. Moreover, sulfur species in fuels can poison the catalysts in fuel cell processors and metal electrodes [7]. Therefore, only fuels with ultra-low sulfur contents are allowed in order to protect the fuel cell system. Typically, the allowable concentrations of sulfur as H₂S and COS for proton exchange membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) are 0.1 and 1 ppm respectively [8].

Conventional hydrodesulfurization (HDS) technology has been widely used in refineries. Most the low sulfur hydrocarbon fuels are directly derived through conventional HDS process [9,10]. Reactions between the light oil and hydrogen are commonly carried out over sulfide catalysts containing Co, Mo and Ni on Al₂O₃ at high temperature (300–450 °C) and under high H₂ pressure (3–5 MPa)

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[11,12]. HDS can efficiently remove aliphatic organic sulfur compounds such as mercaptans, sulfides and disulfides in large scales at relatively low cost. However, typical organosulfur compounds present in high-boiling crude oil fractions are thiophenes, benzothiophenes and their alkylated derivatives, which can be quite stable under conventional HDS conditions [13–15]. In order to efficiently remove organosulfur compounds, more severe conditions are required by HDS including higher H_2 pressure and increase in the reactor size. Therefore, alternative sulfur removal technologies under milder operation conditions have been investigated to replace traditional hydrodesulfurization, such as oxidative desulfurization (ODS) [16–18], biodesulfurization (BDS) [5,19], photocatalytic oxidative desulfurization (PODS) [20–23], adsorptive desulfurization (ADS) [24] and photocatalysis-assisted reactive adsorptive desulfurization [25,26]. Among these new technologies, adsorptive desulfurization does not require additional involvements of H_2 or corrosive oxidants. Desulfurization by adsorption can be operated under ambient temperature without the involvement of high-pressure reactors. As a result, adsorptive desulfurization is considered as a potential alternative method for HDS.

Several adsorbents have been evaluated using commercial fuels and reported to have excellent capacities for sulfur removal [27–31]. A majority of these adsorbents have transition metals in reduced states loaded on supports, such as activated carbon, zeolite, TiO_2 , Al_2O_3 and silica. Those π -complexed adsorbents have been widely studied for deep desulfurization by adsorption. Recently, silver supported on TiO_2 and TiO_2 - Al_2O_3 adsorbents with excellent sulfur adsorption capacities for commercial fuels have been developed in our adsorption lab [32–34]. Silver is in its oxidized state in contrast with other π -complexed adsorbents, and silver supported on TiO_2 adsorbents do not require any sulfidation or activation prior to application. The active sites and organosulfur adsorption pathways onto Ag/TiO_2 and Ag/TiO_2 - Al_2O_3 have been characterized and investigated via X-ray Photoelectron Spectroscopy (XPS) [35], Electron Spin Resonance (ESR) [36], *in situ* Infrared (IR) Spectroscopy [37–39]. The mechanism for sulfur compounds adsorbed on Ag/TiO_2 and Ag/TiO_2 - Al_2O_3 at room temperature has been postulated by the interaction between sulfur molecules and acidic $Ti(IV)$ -OH groups on TiO_2 surface. The influence of surface hydroxyl groups on photocatalytic activities was studied and confirmed using TiO_2 [40]. Thus, sulfur removal capacity of Ag/TiO_2 is related to the photocatalytic activity of TiO_2 .

The chemical state change of Ag caused by UV irradiation was confirmed by XPS. Effects of H_2O molecules and photo-irradiation on surface $Ti(IV)$ -OH groups were characterized by *in situ* IR.

2. Experimental

2.1. Adsorbent preparation

Anatase TiO_2 (ST61120) was purchased from Saint Gobain Norpro as 3.2 mm pellets. The pellets were crushed and sieved down to 850–1400 μm followed by drying in a convection oven for at least 6 h at 110 °C. Calcined TiO_2 samples were obtained by heating the dry TiO_2 particles in a tube furnace at 450 °C in flowing dry air for 2 h.

The aqueous $AgNO_3$ solution was used as the silver precursor to disperse silver onto dry TiO_2 supports by means of incipient wetness impregnation. Crystalline silver nitrate was purchased from Alfa Aesar. The concentration of the impregnating solution was adjusted to obtain the required metal loading on the support. Silver weight loading on the adsorbent was maintained at 4 wt% for Ag/TiO_2 . The resulting particles were dried in the convection oven at 110 °C for 6 h followed by calcination in flowing air at 450 °C for another 2 h.

2.2. Model fuel

Benzothiophene and *n*-octane were purchased from Alfa Aesar and Acros Organics respectively and were used for model fuel preparation. For breakthrough experiments carried out in a fixed bed reactor, model fuels containing 3500 ppmw total sulfur were prepared by mixing benzothiophene with *n*-octane. 1000 ppmw distilled water was added to the model fuel to study the effect of H_2O on desulfurization performance during the sulfur adsorptive procedure.

2.3. UV light sources

Compact ultraviolet (UV) lamps used during photo-assisted ADS were purchased from UVP, LLC. The 4 W UV source is at 365 nm. Light intensity from the UV lamp was measured by a UVX-36 radiometer with a measurement range from 0 to 20 mW/cm². The UVX-36 radiometer was provided with a specific sensor for measuring the irradiation at 365 nm. Typical irradiation intensity at 1 cm from the compact UV lamp was 1.8–2.0 mW/cm². UVL-28 UV lamp ($\lambda = 365$ nm) from UVP was placed in the XPS fast entry load lock. The light intensity on the sample's surface inside the load lock was 1.2 mW/cm².

2.4. Breakthrough experiments

Effects of UV irradiation and H_2O on desulfurization performance of calcined TiO_2 and 4 wt% Ag/TiO_2 adsorbents were evaluated by dynamic sulfur adsorption experiments. The UV-assisted sulfur adsorption apparatus and thermal regeneration unit are illustrated in Fig. 1. The weight loading of adsorbent was kept at 10.0 g for each test. The inner diameter and length of the quartz tube reactor were 16 mm and 62 mm respectively. The reactor bed was first treated with dry N_2 for 1 h in order to remove moisture and impurities before each sulfur adsorption step. Model fuel was then pumped into the quartz reactor tube by a peristaltic pump at a flow rate of 0.5 mL/min with the UV lamps on. Also, desulfurization breakthrough tests without UV irradiation were carried out under darkness. The bed output samples were collected at regular time intervals and analyzed by Antek Sulfur Analyzer. The effect of UV on sulfur removal process was evaluated by comparing the results got from breakthrough experiments with and without UV.

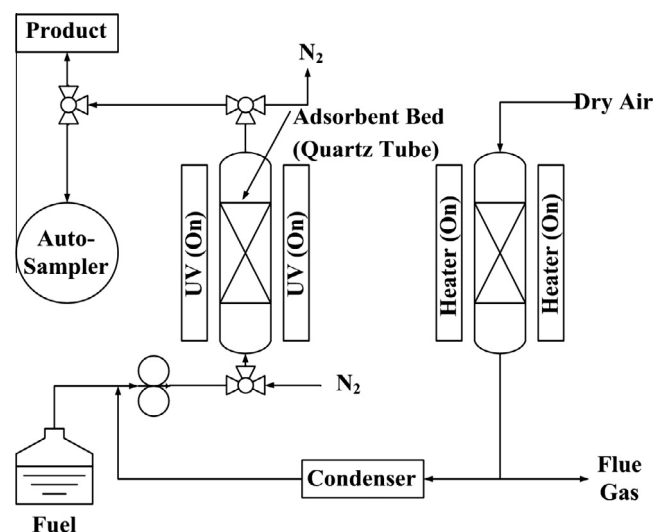


Fig. 1. Photo-assisted sulfur adsorption apparatus and the thermal regeneration unit.

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