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Selective adsorption of thiophenic compounds from fuel over TiO_2/SiO_2 under UV-irradiation

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HIGHLIGHTS

- TiO_2/SiO_2 was developed for selective adsorption of DBTs under UV irradiation.
- Remarkable adsorption uptake and selectivity were achieved for deep desulfurization.
- Introduction of TiO_2 into SiO_2 enhanced its adsorption for $DBTO_2$.
- Adsorption mechanism using TiO_2/SiO_2 under UV irradiation was elucidated.

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ABSTRACT

This study investigates selective adsorption of thiophenic compounds from fuel over TiO_2/SiO_2 under UV-irradiation. The TiO_2/SiO_2 adsorbents were prepared and then characterized by N_2 adsorption, X-ray diffraction and X-ray photoelectron spectroscopy. Adsorption isotherms, selectivity and kinetics of TiO_2/SiO_2 were measured in a UV built-in batch reactor. It was concluded that (a) with the employment of UV-irradiation, high organosulfur uptake of 5.12 mg/g was achieved on the optimized $0.3TiO_2/0.7SiO_2$ adsorbent at low sulfur concentration of 15 ppmw-S, and its adsorption selectivity over naphthalene was up to 325.5; (b) highly dispersed TiO_2 served as the photocatalytic sites for DBT oxidation, while SiO_2 acted as the selective adsorption sites for the corresponding oxidized DBT using TiO_2 as a promoter, the two types of active sites worked cooperatively to achieve the high adsorption selectivity of TiO_2/SiO_2; (c) The kinetic rate-determining step for the UV photocatalysis-assisted adsorptive desulfurization (PADS) over TiO_2/SiO_2 was DBT oxidation; (d) consecutive adsorption-regeneration cycles suggested that the $0.3TiO_2/0.7SiO_2$ adsorbent can be regenerated by acetonitrile washing followed with oxidative air treatment. This work demonstrated an effective PADS approach to greatly enhance adsorption capacity and selectivity of thiophenic compounds at low concentrations for deep desulfurization under ambient conditions.

1. Introduction

Thiophenic compounds in fuel converts to SO_x during combustion, which is harmful to the stratospheric zone and leads to the aerosol of sulfuric acid that causes acid rain [1]. Moreover, thiophenic compounds in fuel poisons the exhaust gas treatment catalysts in vehicles, which causes the release of CO, NO_x, and particulate matter to the environment [2]. Due to the severe environmental impacts from sulfur in fuels, the governments worldwide call for the production and the use of ultra-clean fuels with low sulfur content, i.e., less than 10 and 15 ppmw-S in diesel in Europe and United States [3]. Therefore, the selective removal of thiophenic compounds from fuel has become an increasingly important subject in both academic and refinery communities.

Among the current desulfurization technologies, adsorptive desulfurization (ADS) has been considered as one of the most

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promising approaches, especially aiming at the production of ultra-low-sulfur fuels [4]. In the past decades, extensive studies have been carried out seeking for effective adsorbents for ADS, taking advantages of the porous structure and tunable functionalities of adsorbents. Hernandez-Maldonado et al. [5] pioneered Cu^+ and Ag^+ exchanged zeolites as π-complexation adsorbents for the adsorptive removal of thiophenic compounds from diesel. Favre-Reguillon et al. [6] prepared tetranitrofluorenone- grafted π-acceptor polymers for adsorptive removal of polyaromatic thiophenic compounds in fuel. Zhou et al. [7] studied carbon adsorbents for the adsorption of thiophenic compounds from fuel, and reported that the acidic oxygen functionalities on carbon surface were involved towards desulfurization. Bandosz et al. [8] prepared polymer-derived carbons for desulfurization and reported that the presence of the acidic groups on carbons may cause the oxidation or reactive adsorption of thiophenic compounds. As an emerging type of porous inorganic-organic hybrids, metal organic frameworks (MOFs), such as UMCM-150 [9], MIL-47 [10], Cu-BTC [11], etc., and functional MOFs, such as Cu^+ loaded MIL-101(Fe) [12] and phosphotungstic acid loaded Cu-BTC [13] were developed for the removal of thiophenic compounds from fuel, which achieved high adsorption capacities. Progresses have been made on developing new adsorbents for the removal of thiophenic compounds in fuel, however, most of the adsorbents cannot survive or work effectively for real fuel desulfurization due to the strong competition from polyaromatic hydrocarbons (can be 5–10 wt.%) with the trace amount of thiophenic compounds (<15 ppmw-S) in fuel [14]. Therefore, the development of new approaches with enhanced adsorption selectivity of thiophenic compounds has becoming more critical in ADS.

Metal oxide-based adsorbents have caught attentions with plausible regenerability by air oxidation treatment [15]. Watanabe et al. [16] developed regenerable mixed TiO_2–CeO_2 adsorbent that demonstrated high ADS capacity from real fuel, and the adsorption selectivity was enhanced by tuning the Ti/Ce ratio. Recently, Xiao et al. [17] reported a two-step ADS approach using TiO_2–CeO_2/MCM-48 adsorbent for selective removal of thiophenic compounds in light-irradiated diesel, which achieved a high desulfurization capacity (1.143 mg-S per g-Ads) of 14.5 ppmw-S real diesel, and the enhanced adsorption selectivity of thiophenic compounds was due to the conversion of low-polar thiophenic compounds to the corresponding polar sulfones on the adsorbent [15]. Previous work suggested that converting thiophenic compounds to sulfones over an adsorbent can be an effective approach to enhance ADS selectivity.

With this in mind, herein, a dual-functional $x\mathrm{TiO_2}/(1-x)\mathrm{SiO_2}$ adsorbent was developed for selective ADS of fuel under UV-irradiation. The TiO_2/SiO_2 acted as both a photocatalyst (to chemically shift thiophenic compounds to the corresponding oxidized thiophenic compounds under UV at ambient conditions), and meanwhile an adsorbent (to selectively adsorb the oxidized thiophenic compounds under ambient conditions). The adsorption of thiophenic compounds over $x\mathrm{TiO_2}/(1-x)\mathrm{SiO_2}$ adsorbents under UV-irradiation were studied in a batch reactor coupled with a built-in mercury lamp. The adsorbents were characterized by N_2 adsorption, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The adsorption isotherms of dibenzothiophene (DBT) under UV-irradiation were fitted to isotherm models, and compared to other types of desulfurization adsorbents. The adsorption selectivities of dibenzothiophene sulfone ($DBTO_2$) and thiophenic compounds referred to aromatic naphthalene in fuel were calculated. The adsorption kinetics of $0.3TiO_2/0.7SiO_2$ for thiophenic compounds under UV-irradiation were investigated and modeled. Effects of Ti/Si ratio in $x\mathrm{TiO_2}/(1-x)\mathrm{SiO_2}$ adsorbents and ADS temperature were investigated. Additionally, regeneration of $0.3TiO_2/0.7SiO_2$ was further discussed.

2. Experimental

2.1. Adsorbent syntheses

A series of $x\mathrm{TiO_2}/(1-x)\mathrm{SiO_2}$ with varied Ti/Si molar ratio (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0) were prepared using a sol–gel method [18]. The mixture of certain amounts of titanium ethoxide (TNBT, $Ti(OC_2H_5)_4$, Aldrich), tetraethylorthosilicate (TEOS, 98%, Adrich), and acetic acid was dissolved in ethanol (99.5%, Aldrich) as solution A. The solution B was prepared by dissolving nitric acid (70%, Aldrich) solution (added distilled water) was mixed with ethanol as solution B. The weight ratio of (TEOS + TNBT):EtOH:H_2O:CH_3COOH:HNO_3 was 1:20:7:2:0.01. Solution B was added into solution A drop by drop, and the transparent sol was formed, then the mixture was ramped to 50 °C to form gel. After that, the gel was dried at 80 °C for 48 h, and calcined at 400 °C for 4 h. The prepared $x\mathrm{TiO_2}/(1-x)\mathrm{SiO_2}$ samples were then stored in a desiccator for use.

SiO_2 (A-type) with S_{BET} of 450 m^2/g was provided by Sigma–Aldrich, MCM-48 with S_{BET} of 1281 m^2/g was synthesized in lab using hydrothermal method [19], and MCM-41 with S_{BET} of 1200 m^2/g was provided by Zhuoyue Chemicals, Shanghai. Two types of metal organic frameworks (MOFs), Cu-BTC (S_{BET} of 1024 m^2/g) and MIL-100(Fe) (S_{BET} of 1907 m^2/g) were prepared in lab using the hydrothermal methods [11].

2.2. Model fuels (MDFs)

The model fuels for the adsorption kinetics and isotherm studies of thiophenic compounds were prepared by dissolving given amounts (100–400 ppmw) of dibenzothiophene (DBT, 98%) in dodecane (99%). The model fuels for the adsorption selectivity study were prepared by dissolving the same molar concentration (3.12 μmol/g) of each single compound, including naphthalene (Nap, 99%), benzothiophene (BT, 99%), dibenzothiophene (DBT, 98%), 4-methyldibenzothiophene (4-MDBT, 96%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 97%), and dibenzothiophene sulfone ($DBTO_2$, 97%), respectively, in solvents (solvent 1—toluene; solvent 2–40 wt.% toluene in 60 wt.% dodecane; and solvent 3—dodecane). All the chemicals were purchased from Sigma–Aldrich and used without further purification.

2.3. Adsorption experiments

Adsorption of thiophenic compounds under UV-irradiation. The adsorption experiments were carried out in a batch reactor setup under ambient conditions. The adsorption experiments were carried out in a batch reactor setup as showed in Fig. S1. Firstly, the adsorbents and model fuels were mixed in the reactor, then a water-cooled condenser was installed above the reactor to avoid liquid loss (~3%). After that, air was flowed in and the UV lamp (built-in 400 W high pressure mercury lamp, Leman, China) was switched on to make the PADS begin. The treated fuels were sampled periodically. The ADS experiments were carried out at the air flow rate of 20 cc/min and fuel-to-sorbent ratio (w/w) of 20 in general. The fuel-to-sorbent ratio (w/w) of 70 was used for the DBT adsorption isotherm study over $0.3TiO_2/0.7SiO_2$ with and without UV-irradiation, as well as Cu-BTC and MIL-100(Fe). The sulfur concentrations in initial and desulfurized fuels were monitored using an Antek 9000 series total sulfur analyzer. The concentrations of other compounds in the treated model fuel samples were analyzed by a high-performance liquid chromatogram (HPLC) equipped with a UV–vis detector at 301 nm and an ODS-C18 column at the flow rate of 1.0 $cm^3\,min^{-1}$. TiO_2/SiO_2 samples tested with and without UV-irradiation were denoted as TiO_2/SiO_2-UV and TiO_2/SiO_2, respectively.