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Catalytic adsorptive desulfurization of model diesel fuel using TiO_2/SBA-15 under mild conditions

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HIGHLIGHTS

- Proposed a new CADS–TiO_2/SBA-15 system for ultra-deep desulfurization of fuel.
- High CADS capacity of 12.7 mg/g at low S-conc. of 15 ppm-S was achieved.
- Fast CADS kinetic equilibrium was achieved in 0.5 h.
- Excellent regenerability of TiO_2/SBA-15 by oxidative air treatment was reported.

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ABSTRACT

This study investigates catalytic adsorptive desulfurization (CADS) of model diesel fuel using TiO_2/SBA-15 under mild conditions. The TiO_2/SBA-15 was prepared by a facile incipient wetness impregnation method and characterized by N_2 adsorption and X-ray diffraction. The CADS referred to ADS performance were evaluated in a batch reactor. High desulfurization uptake of 12.7 mg/g was achieved at low sulfur concentration of 15 ppmw-S by TiO_2/SBA-15 under CADS, which was two-magnitude higher than that under ADS without the in-situ catalytic oxidation of dibenzothiophene. Kinetic results suggested that the CADS equilibrium over TiO_2/SBA-15 was reached fast in 0.5 h. In the CADS–TiO_2/SBA-15 system, the TiO_2 loading, cumene hydroperoxide/dibenzothiophene ratio and CADS temperature were optimized to be 10 wt%, 2, and 35 °C, respectively. Furthermore, desulfurization tests in 5 consecutive CADS-regeneration cycles suggested that the bi-functional TiO_2/SBA-15 can be regenerated by acetonitrile washing followed with oxidative air treatment. The CADS–TiO_2/SBA-15 mechanism went through the oxidation of DBT to oxidized $DBTO_2$ over TiO_2/SBA-15 by cumene hydroperoxide, which was followed by the adsorption of the oxidized $DBTO_2$ over TiO_2/SBA-15. The superior desulfurization uptake at low sulfur concentration range, fast adsorption kinetics, excellent regenerability, operation at mild conditions, and facile and low-cost adsorbent synthesis make the CADS–TiO_2/SBA-15 system an effective and economic desulfurization approach for ultra-clean fuel production.

1. Introduction

Ultra-clean fuel production has attracted widespread attention globally due to the intensified environmental and health concerns [1,2]. To mitigate the hazards initiated by the organosulfur compounds in fuels, i.e. dibenzothiophene (DBT) and its derivatives, stringent environmental regulations have been introduced worldwide to reduce the sulfur content in fuel, i.e. less than 10 and 15 ppmw-S in diesel in Europe and United States [3,4]. The more and more strict regulations to limit the S-level in fuel have brought a major challenge for the petroleum refining industry. At such scenario, ultra-deep desulfurization of fuels has become an increasingly important subject worldwide.

In refinery, desulfurization is achieved by hydrodesulfurization (HDS) or hydrotreating process at the operation temperature over 300 °C and hydrogen pressure at 20–100 atm using the CoMo- or NiMo-based catalyst [5–8]. HDS is efficient to remove thiols, sulfides and disulfides, but turns to be less energy- and economy-effective to removal refractory sulfur compounds, i.e. DBT and its derivatives for ultra-deep desulfurization of fuel [9,10]. Therefore, complementary desulfurization technologies to effectively remove refractory sulfur compounds at low concentration is demanded for ultra-clean fuel production.

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With the advantages of deeply removing refractory sulfur compounds under ambient conditions, adsorptive desulfurization (ADS) has been considered as a promising approach for ultra-deep desulfurization, in which adsorbents play the key role. Extensive studies have been carried out on developing ADS adsorbents via either enhancing the porosity or tuning functionality of adsorbents to host thiophenic compounds. Reported plausible adsorbents include Cu^+ and Ag^+ exchanged zeolites [11–13], tetranitro-9-fluorenone grafted polymers [14,15], acidic oxygen functional groups modified carbon materials [16–18], metal organic frameworks [19–21], metal oxides [22,23], zero-valence metals [24], aluminosilicates [25], etc. The involved ADS mechanisms were elucidated as π-complexation, π-acceptor–donor interaction, π–π & H-bonding interaction, metal–S chemisorption, chemisorbed oxygen–sulfur interaction, Van der waals interaction, etc. [26–30] Though significant progresses have been made on developing new adsorbents for ADS of fuels, most of the adsorbents were not effective for ultra-deep desulfurization of real fuels, as the strong competitive components, i.e. polyaromatic hydrocarbons and nitrogen compounds present in real fuels was neglected. Therefore, developing highly selective ADS processes is critical to mitigated competitive adsorption for effective ultra-deep desulfurization of fuels.

Recently, a coupling oxidation-adsorption process was developed for selective ADS, where organosulfur compounds was firstly oxidized to sulfoxides or sulfones and then selectively adsorbed on the same adsorbent (also acted as oxidation catalyst). Xiao et al. [31,32] firstly reported a catalytic ADS system of diesel using TiCeO mixed metal oxides for ultra-deep desulfurization, and clarified the selective ADS mechanism as chemically converting thiophenic compounds to highly polar sulfoxides over the TiCeO adsorbent. Wang et al. [33] investigated a UV-photocatalytic ADS system using TiO_2/SiO_2. High organosulfur uptake of 5.12 mg/g was achieved on the $0.3TiO_2/0.7SiO_2$ adsorbent at low sulfur concentration of 15 ppmw-S, and its adsorption selectivity over naphthalene was up to 325.5. Shen et al. [34] synthesized TS-1 on porous glass beads for catalytic ADS, and reported high catalytic oxidation activity and good stability of the composite material. Previous work demonstrated that catalytic ADS (CADS) via in-situ converting thiophenic compounds to sulfones over an adsorbent can be a plausible approach to enhance ADS selectivity for ultra-deep desulfurization. Therefore, further development of facile CADS processes with superior deep-desulfurization efficiency and low capital cost will push the ADS technology forward for real applications.

In this work, a facile CADS process using TiO_2/SBA-15 with cumene hydroperoxide (CHP) under mild conditions was proposed and systematically investigated. The TiO_2/SBA-15 was prepared by the facile incipient wetness impregnation method and characterized by N_2 adsorption and X-ray diffraction. The CADS referred to ADS performance of TiO_2/SBA-15 were measured in a batch reactor. The CADS isotherm of TiO_2/SBA-15 was fitted to Langmuir isotherm model, and compared to its sole ADS isotherm without in-situ catalytic reaction. Moreover, the CADS kinetics of TiO_2/SBA-15 was investigated and modeled. Effects of TiO_2 loading, CHP/DBT ratio and CADS temperature were optimized. Additionally, the regeneration of TiO_2/SBA-15 was further discussed.

2. Experimental

2.1. Adsorbent syntheses

The supported TiO_2/SBA-15 adsorbents with various TiO_2 loading (1, 5, 10, 15 wt.%) were prepared by incipient wetness impregnation assisted with ultrasound [24]. In a typical synthesis, given amount of tetrabutyl titanate (AR, Shanghai Lingfeng Chemicals Co.) was dissolved in 3 ml of ethanol (AR, Guangdong Chemicals Co.), and then the mixture was added into 1 g of SBA-15 (Shanghai Xianfeng Chemicals Co.) drop by drop under ultrasound. After that, the slurry was dried at 40 °C for 2 h while stirring. The sample was then calcined under flow at 400 °C for 4 h ramped at 1.5 °C/min. The as-prepared TiO_2/SBA-15 adsorbents were stored in desiccator before use. The samples were denoted as 1%TiO_2/SBA-15, 5%TiO_2/SBA-15, 10%TiO_2/SBA-15, and 15% TiO_2/SBA-15, respectively.

2.2. Model fuels (MDFs)

The MDFs were prepared by dissolving given amounts (100–800 ppmw-S) of dibenzothiophene (Sigma-Aldrich, DBT, 98%) in dodecane (AR, Guangdong Guanghua Chemicals Co., 99%). Certain amount of cumene hydroperoxide (CHP, Aladdin, 80%) based on the calculation of given CHP/DBT molar ratio was added into the model fuel for CADS experiments.

2.3. Adsorption experiments

The adsorption experiments were carried out in a batch reactor setup. The DBT and $DBTO_2$ concentrations in the initial and desulfurized fuel samples were monitored 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/SBA-15 samples tested under CADS (with the additional CHP) and ADS (without CHP) system were denoted as CADS–TiO_2/SBA-15 and ADS–TiO_2/SBA-15, respectively.

The CADS adsorption isotherms of DBT were carried out in a stirred batch system. About 0.03 g of adsorbent, 2.7 g of model fuel (50, 100, 150, 200, 250, 300 ppm-S of DBT in dodecane, and CHP at the O/S (cumene hydroperoxide versus DBT) ratio of 2:1 were mixed at 35 °C until reached adsorption equilibrium (2 h). The treated fuels were sampled and tested using a HPLC equipped with a UV–vis detector at 301 nm.

2.4. Regeneration of TiO_2/SBA-15

Besides adsorption capacity and selectivity, regenerability is an important parameter for adsorbents to be considered for practical applications. The spent TiO_2/SBA-15 adsorbent was regenerated by oxidative air treatment. In the regeneration process, firstly, the spent adsorbent was washed with excess amount of acetonitrile and filtered. The solid was dried and then calcined at 400 °C for 4 h ramped at 1.5 °C/min. After that, the sample was stored in a desiccator before tested in the next desulfurization cycle.

2.5. Characterization of TiO_2/SBA-15

The BET surface area (S_{BET}) were measured by nitrogen adsorption/desorption at −196 °C using an ASAP2020 analyzer (Micromeritics). Prior to each measurement, the samples were outgassed at 150 °C for 12 h. X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54056$ nm) operated at 40 mA and 40 kV at a scanning range of 10–80° following Joint Committee on Powder Diffraction Standards (JCPDS). Transmission electron microscopy (TEM) was conducted using a JEOL2100F. Fourier transform infrared spectra (FT-IR) of the samples were recorded using an IR Affiniy-1 FTIR spectrometer.