

One-pot photocatalysis-assisted adsorptive desulfurization of diesel over doped-TiO₂ under ambient conditions

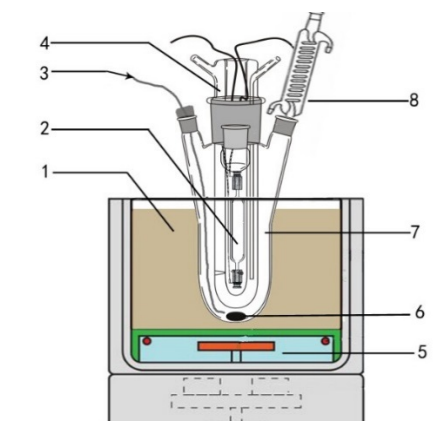
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Experimental

A series of Ti_{1-x}Si_xO₂ adsorbents with varied Ti/Si molar ratio (10/0, 9/1, 7/3, 5/5, 3/7, 1/9, 0/10) were prepared by a sol-gel method. Given amounts of titanium ethoxide (TNBT, Ti(OC₂H₅)₄, Ti-20% Aldrich), tetraethylorthosilicate (TEOS, 98% Aldrich), and acetic acid were mixed and dissolved in ethanol (99.5%, Aldrich), which was denoted as solution A. Given amounts of nitric acid (70%, Aldrich) and distilled water were mixed and dispersed into ethanol, which was denoted as solution B. The weight ratio of (TEOS+TNBT): EtOH: H₂O: CH₃COOH: HNO₃ was set as 1: 20: 7: 2: 0.01. A transparent sol was formed by doping solution B into solution A drop by drop, and then settled at 50 °C forming gel. The gel was then dried at 80 °C for 48 h, and then calcined at 400 °C for 4 h. BET surface area (S_{BET}) was characterized by N₂ adsorption test at 77 K using an ASAP 2020 analyzer (Micromeritics). For comparison, Ti_{0.9}Ce_{0.1}O₂ metal oxides (prepared by a urea precipitation method³, S_{BET} of 249 m²/g); P25 TiO₂ (Degussa, S_{BET} of 56 m²/g), TS-1 (Shentan Chemicals, Shanghai, S_{BET} of 320 m²/g), and MCM-41 (Zhuoyue Chemicals, Shanghai, S_{BET} of 1200 m²/g), were used as references.

The real diesel with 220 ppmw-S was provided by Guangdong Petrochemical Corporation. The model fuel was prepared by dissolving 320 ppmw-S of dibenzothiophene (DBT, Sigma-Aldrich, 98%) into tetrahexane (Sigma-Aldrich, 99%).

ADS experiments were carried out in a batch reactor setup with the schematic diagram as shown in Figure S1. A water-cooled condenser was installed above the batch reactor to avoid liquid loss (~3%). Ti_{1-x}Si_xO₂ adsorbent and fuel were mixed in the reactor (fuel-to-adsorbent weight ratio of 10 for real diesel, and 20 for model fuel), a constant air flow at 10 ml/min was bubbled into the adsorbent/fuel mixture. UV light irradiation was provided by a built-in 400 W high pressure mercury lamp (Leman, China). The treated fuels were sampled periodically (terminated in 6 h). The sulfur concentrations in initial and desulfurized fuels were monitored using an Antek 9000 series total sulfur analyzer. Sulfur species in treated fuels were qualified using a HP 5890 gas chromatograph (XTI-5 column from Restek, 30 m × 0.25 mm) equipped with a pulsed flame photometric detector (PFPD). To identify the sulfur species on the spent Ti_{1-x}Si_xO₂ adsorbent, a polar solvent of acetonitrile (Sigma-Aldrich, 99.8%) was used to wash the spent adsorbent, and the eluent was characterized by a gas-chromatograph/mass spectrometer (GCMS-QP 2010, SHIMADZU) equipped with capillary DB-1 (30 m × 0.25 mm × 1 μm). The detailed temperature program setup was reported elsewhere¹.



1-oil bath; 2-built-in lamp; 3-air inlet; 4-condensing interlayer; 5-blender; 6-stirrer bar; 7-fuel; 8-condenser

Figure S1. Schematic diagram of the batch reactor setup for photocatalysis-assisted ADS of fuel

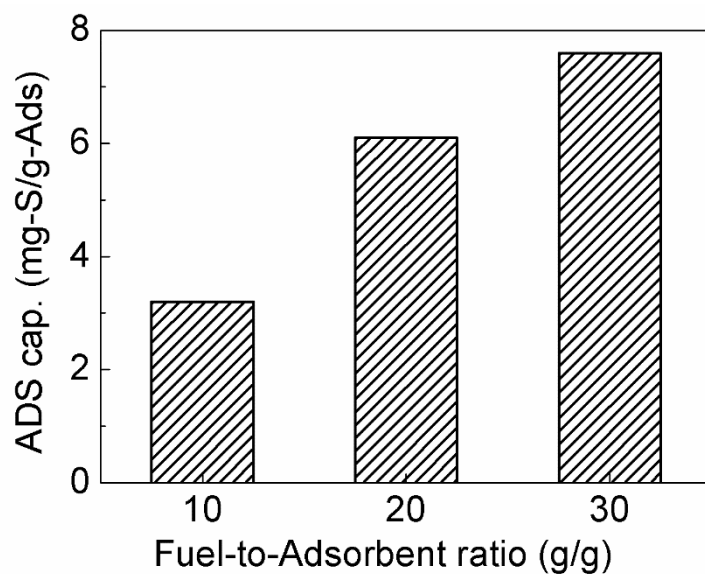


Figure S2. Desulfurization capacities of the $\text{Ti}_{0.3}\text{Si}_{0.7}\text{O}_2$ at different fuel-to-adsorbent ratios

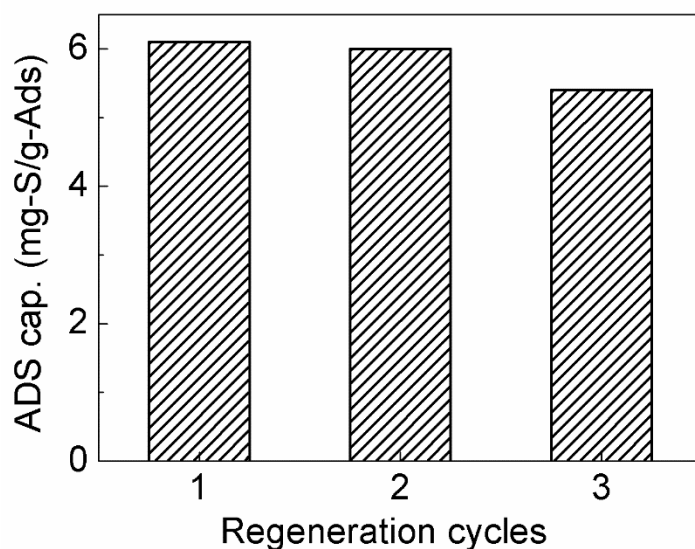


Figure S3. Desulfurization capacities of the $\text{Ti}_{0.3}\text{Si}_{0.7}\text{O}_2$ in the first three regeneration cycles (Regeneration method: the spent Ti-Si-O was washed with excess amount of acetonitrile followed by oxidative air treatment at 400 °C)

References

- 1 W. Zhang, H. Zhang, J. Xiao, Z. X. Zhao, M. X. Yu and Z. Li, *Green Chem.*, 2014, 16, 211–220.