One-pot Photo-oxidative Adsorption Desulfurization of Dibenzothiophene in Diesel Fuel over TiO_2-ZrO_2

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Introduction

In desulfurization of diesel fuel, 4,6-dimethyldibenzothiophene (4,6-DMDBT) is known as a refractory sulfur compound. To produce ultra-low sulfur diesel fuel (< 5 ppmS), this compound needs to be removed. Unfortunately, the current hydrodesulfurization process (HDS) is still not efficient for ultra-deep desulfurization due in part to the steric hindrance of the bulky sulfur compounds. Combining two promising alternative approaches, adsorptive desulfurization (ADS) and oxidative desulfurization (ODS), might improve total desulfurization of diesel fuel since ODS reactivity increases as the electron density of sulfur atom increases, allowing easier removal of 4,6-DMDBT while ADS can selectively remove dibenzothiophenes (DBTs) against aromatic hydrocarbons in real diesel fuel [1, 2]. In this work, a novel desulfurization process called one-pot photo-oxidative adsorptive desulfurization (OPAD) was explored, which involves both ODS and ADS under UV/Vis light irradiation using TiO_2-ZrO_2 mixed-metal oxides as an adsorbent and photocatalyst.

Materials and Methods

Titanium (IV) oxide, zirconium (IV) oxide, their mixed oxides, and titanium (IV) cerium (IV) mixed oxides were prepared by applying urea (co)precipitation method. Calcination was carried out at 400 °C for 2 h under air. Desulfurization tests were run in batch system at 30 °C under air bubbling with flow rate of 2.8 ml/min, stir speed of 500 rpm and UV/Vis light. Dibenzothiophene in diesel (DBT/Diesel) with sulfur concentration of ~400 ppm was used as an initial fuel. Gas Chromatography-Pulsed Flame Photometric Detector (GC-PFPD) and Total S-analyzer (ANTEK model 9000) were used for sulfur analysis.

Results and Discussion

Figure 1 illustrates the comparison of S-concentrations achieved after desulfurization using $Ti_{0.9}Zr_{0.1}O_2$, TiO_2, ZrO_2, and $Ti_{0.9}Ce_{0.1}O_2$. $Ti_{0.9}Ce_{0.1}O_2$ was one of the best adsorbents for 4,6-DMDBT in diesel fuel developed by our research group [3]. It turned out that the $Ti_{0.9}Zr_{0.1}O_2$ showed the best DBT removal among all the metal oxides.

Figure 2 demonstrates the change in total sulfur concentrations with time of treated fuels under different desulfurization processes. As seen in the 2-step desulfurization, the presence of $Ti_{0.8}Zr_{0.2}O_2$ after light irradiation (6-23h) could not lower sulfur level as low as the treated fuel from neither 1-step desulfurization nor 3-step desulfurization. The DBT-sulfone generated in fuel and adsorbed on $Ti_{0.8}Zr_{0.2}O_2$ surface was confirmed by GC-PFPD analysis. From the results, it is feasible that the $Ti_{0.8}Zr_{0.2}O_2$ might not only act as a sulfone adsorbent but also a photocatalyst for sulfone generation, which might facilitate the desulfurization to a deeper level compared to process that has either light or $Ti_{0.8}Zr_{0.2}O_2$.

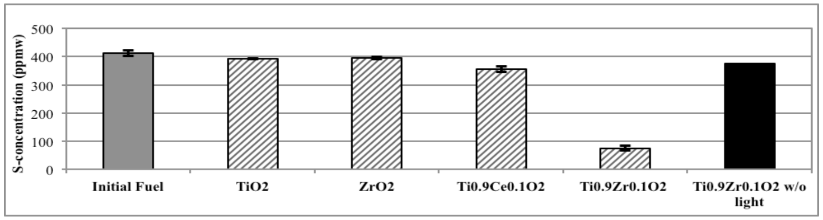

Figure 1. Total sulfur concentrations of initial- (DBT/Diesel) and treated fuels using different (mixed) metal oxides. Desulfurization was studied under the same condition with light irradiation, except the last column which was performed without light. Fuel/metal oxide ratio, 10 ml/0.5g. Test time, 6 h.

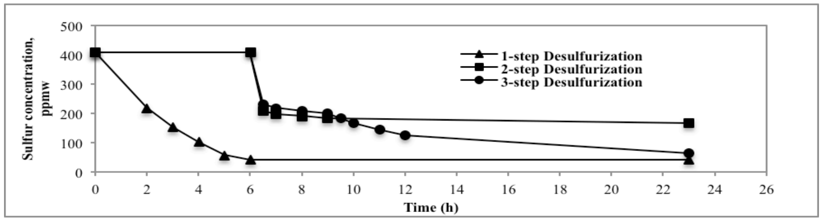

Figure 2. Change in total sulfur concentrations with time of treated fuels under different desulfurization processes. *1-step desulfurization* (▲): light+$Ti_{0.8}Zr_{0.2}O_2$ from 0-23 h. *2-step desulfurization* (■): light+no $Ti_{0.8}Zr_{0.2}O_2$ from 0-6 h; no light+$Ti_{0.8}Zr_{0.2}O_2$ from 6-23 h. *3-step desulfurization* (●): light+no $Ti_{0.8}Zr_{0.2}O_2$ from 0-6 h; no light+$Ti_{0.8}Zr_{0.2}O_2$ from 6-9 h; light+$Ti_{0.8}Zr_{0.2}O_2$ from 9-23 h. Fuel/$Ti_{0.8}Zr_{0.2}O_2$ ratio of 20ml/1g.

Significance

The OPAD was found to be feasible for dibenzothiophene removal from diesel fuel. Addition of ZrO_2 into TiO_2 dramatically improved the desulfurization, and the mixed-metal oxides TiO_2-ZrO_2 is likely to act as both a photocatlayst and an adsorbent for sulfone.

References

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