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A Novel Approach for Ultra-Deep Adsorptive Desulfurization of Diesel Fuel over TiO_2–CeO_2/MCM-48 under Ambient Conditions

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Significance

A novel approach for ultra-deep desulfurization of diesel fuel was proposed, in which the original fuel was treated by light irradiation before adsorptive desulfurization (ADS) over the TiO_2–CeO_2/MCM-48 adsorbent under ambient conditions. A superior capacity of 95 cm^3-fuel/g-adsorbent (32 times higher than that of the original fuel) was achieved. The promoting effect of light irradiation was likely through in situ peroxides generation in fuel under visible light/sunlight, which may oxidize organosulfur to form strongly adsorbed sulfones over the adsorbent.

Keywords: desulfurization, adsorption, fuel, light irradiation

Sulfur impurities in diesel fuel have caused concerns because they are converted to SO_x after combustion, which not only results in acid rain but also poisons the catalysts in the exhaust gas converter for abating CO, NO_x, and particulate matter.[1] Since 2006, US EPA regulations have required the sulfur content in diesel fuel to be less than 15 parts per million by weight (ppmw). Meanwhile, the sulfur content in crude oils is getting higher and higher. Due to the discrepancy between the high-sulfur content in the crude oils and the required low-sulfur content in liquid fuels, desulfurization has become a more serious task. Some promising applications require even more stringent constraint on sulfur content, that is, proton-exchange membrane fuel cells can only tolerate <1 ppmw-S to avoid the poisoning of reforming catalysts, water gas shift catalysts, and electrode catalysts.[2] Therefore, ultra-deep desulfurization for the production of ultra-clean diesel fuel with <1 ppmw-S becomes an important research subject worldwide. For ultra-deep desulfurization of diesel fuel, the commercial desulfurization technology in refinery, hydrotreating, becomes less efficient and energy intensive as it requires much larger catalyst bed, higher temperature and pressure, and more hydrogen to remove refractory sulfur compounds, that is, the major sulfur compound 4,6-dimethyldibenzothiophene (4,6-DMDBT) in diesel.[3] As a complement, adsorptive desulfurization (ADS), using solid adsorbents to remove sulfur compounds in fuels via selective adsorption, has attracted significant attention for ultra-deep desulfurization. ADS can be carried out under mild conditions without using costly hydrogen and has the capability to reduce sulfur content to <1 ppmw. ADS adsorbents for liquid fuels desulfurization include π-complexation adsorbents,[4–6] immobilized π-acceptor adsorbents,[7] metal organic frameworks,[8] Ni-based adsorbents,[9] carbon adsorbents,[10–12] aluminosilicates,[13] and so on. However, most of the adsorbents are not effective for diesel fuel due to (a) the steric hindrance of alkylated sulphur compounds,[14,15] (b) and/or the competitive adsorption between the trace amount of sulfur compounds (<15 ppmw) and the relatively large amount of polyaromatics (about 5–10 wt %).[16] Therefore, it is highly desired to develop new selective ADS adsorbents and processes for the production of ultra-clean diesel fuel (<1 ppmw-S) from current commercial diesel fuels.

Recently, we have developed air regenerable TiO_2–CeO_2 mixed metal oxides adsorbents for ADS of jet fuels showing good ADS performance.[17,18] Compared to pure TiO_2, the addition of 10 mol % CeO_2 to TiO_2 can significantly enhance the ADS performance by more than doubling the adsorption capacity. Computational studies suggested that oxygen could be chemisorbed on TiO_2 surface, which leads to the formation of a sulfone-like species on O-rich sites.[19,20]

Additional Supporting Information may be found in the online version of this article.

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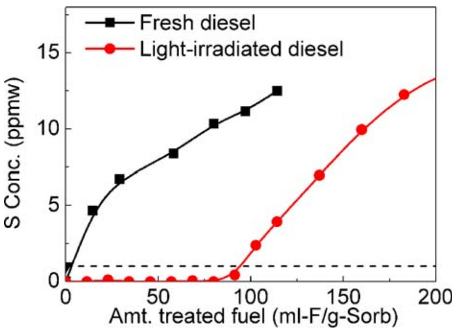

Figure 1. Breakthrough curves of total sulfur compounds over the TiO_2–CeO_2/MCM-48 adsorbent from the original and light-irradiated diesel fuel at 25°C and a LHSV of 9.6 h^{-1}.

[Conditions for light irradiation of fuel: 100 g of fuel in a 250 ml flask, 150 W Xenon lamp, distance (between the lamp and the center of the flask) of 30 cm, air flow rate of 10 ml/min.] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The promoting effect of CeO_2 addition may be attributed to its enhancement in the formation of sulfone-like species, which have higher polarity and are more prone to surface adsorption than the original sulfur compounds.[21] Given that the primary product of hydrocarbon auto-oxidation in petroleum induced by light is peroxides,[22–24] which can be a type of active oxygen species for the formation of sulfone-like species, we thus explored a new approach for selective and ultra-deep desulfurization of diesel fuel by ADS over TiO_2–CeO_2-based adsorbents. In the approach, diesel fuel was first treated by light irradiation, and then applied for ADS over the TiO_2–CeO_2/MCM-48 adsorbent under ambient conditions. The effectiveness of the new approach for selective and ultra-deep desulfurization of diesel fuel was demonstrated in this *Letter*. The adsorption performance was compared and evaluated in a fixed-bed flow adsorption system. The promotion effect of light irradiation was investigated based on detailed sulfur analyses and verified by a model compound study.

The experimental details of TiO_2–CeO_2/MCM-48 adsorbent synthesis, light irradiation treatment of fuel, flow system desulfurization tests, and sulfur analyses were described in Supporting Information. Figure 1 shows the breakthrough curve of total sulfur over the TiO_2–CeO_2/MCM-48 adsorbent from the light-irradiated diesel fuel at room temperature, where the breakthrough curve obtained from the original diesel fuel is also presented for comparison. For the original diesel fuel, the TiO_2–CeO_2/MCM-48 adsorbent exhibited a breakthrough capacity at 1 ppmw-S at around 3 cm^3-F/g-A, which corresponds to 0.036 mg-S/g-A. In sharp contrast, the breakthrough capacity for the light-irradiated diesel fuel was dramatically increased, reaching 95 cm^3-F/g-A or 1.143 mg-S/g-A, 32 times greater than that for the original diesel fuel. The results clearly indicate that light irradiation of diesel fuel before ADS can significantly increase the adsorption capacity of TiO_2–CeO_2/MCM-48 adsorbent for ADS of diesel fuel. Moreover, with the new approach, the ADS capacity can be further improved, which will be addressed in our future work.

The adsorption performance of an adsorbent is determined by the total accessible adsorption sites on the adsorbent, and the interaction between the adsorbent and the adsorbate, which varies with the properties of adsorbent and adsorbate. Over the same TiO_2–CeO_2/MCM-48 adsorbent, the adsorption capacity was significantly improved for the diesel fuel after light irradiation, hinting a significant change in the properties of the adsorbates, that is, the sulfur compounds in the fuel. In order to understand the change of sulfur compounds and the sulfur chemistry involved in the adsorption over TiO_2–CeO_2/MCM-48 adsorbent from light-irradiated diesel fuel, sulfur species in the fuel before and after ADS were examined.

Figure 2 shows the Gas chromatography-pulsed flame photometric detector (GC-PFPD) chromatographs of the original and light-irradiated diesel fuels, and the desulfurized fuel samples from the light-irradiated diesel fuel at different time-on-streams. The original diesel fuel used in this study contained mainly 4,6-DMDBT along with other alkyl-substituted DBTs including 4-E,6-MDBT, 2,4,6-TMDBT, 4,6-DEDBT, and 6-E,2,4-DMDBT, consistent with what has been reported in the literature.[9] The light-irradiated diesel fuel had the same GC-PFPD profile as the original diesel, suggesting that light irradiation did not alter the sulfur compounds in the fuel. For the desulfurized fuel sample collected at the point of 103 cm^3-F/g-A which had a sulfur level of 2.4 ppmw-S, the major sulfur compounds were 4,6-DMDBT and 4-E,6-MDBT. In the GC-PFPD profile of the desulfurized fuel sample collected at the point of 160 cm^3-F/g-A with a sulfur level of 9.5 ppmw, all the sulfur compounds presented in the original diesel appeared. It implies that 4,6-DMDBT and 4-E,6-MDBT broke through earlier than 2,4,6-TMDBT, 4,6-DEDBT, and 6-E,2,4-DMDBT, that is, a lower desulfurization selectivity to 4,6-DMDBT and 4-E,6-MDBT compared to other refractory sulfur compounds with increased number and size of the alkyl substituent groups. The trend is opposite to those reported on Ni-based sorbent for ADS[9] and catalysts for HDS.[15] This may further suggest that the electron density on the conjugated aromatic system, which is influenced by the number and size of the alkyl substituents on DBT, may affect the interaction between the sulfur atom and the active sites on TiO_2–CeO_2/MCM-48.

It is interesting to note that in addition to the initial refractory sulfur compounds in the diesel fuel, some new sulfur species with longer retention time were also observed in the GC-PFPD profile of the desulfurized fuel sample collected at the point of 160 cm^3-F/g-A, which were suggested as sulfone species.[25] The formation of the new sulfur species suggests a possible chemical transformation of sulfur compounds during the adsorption process over the TiO_2–CeO_2/MCM-48 adsorbent. In addition, it is noticeable in Figure 2 that new sulfur species made breakthrough later than initial sulfur species from light-irradiated fuel, due to the stronger adsorption affinity of sulfones with a higher polarity (The dipole magnitude of DBT is 0.901 D, whereas that of $DBTO_2$ is 5.453 D[21]). It should be mentioned that after light irradiation of diesel fuel, the sulfur compounds remain the same as initial sulfur species as shown in the second chromatograph in Figure 2, which suggested that the chemical transformation of sulfur species happened on the TiO_2–CeO_2/MCM-48 surface. The chemical transformation of sulfur species, its effects on

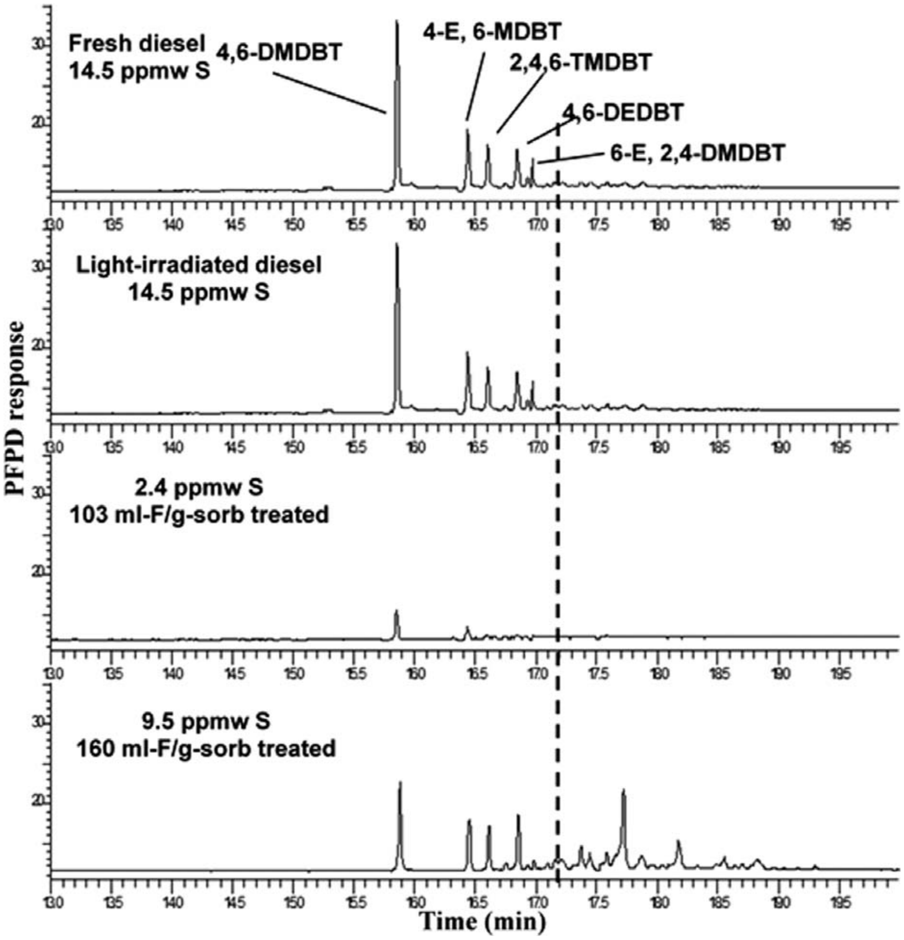

Figure 2. GC-PFPD chromatographs of the original diesel fuel, the light-irradiated diesel fuel, and the collected desulfurized diesel fuel samples over the TiO_2–CeO_2/MCM-48 adsorbent from light-irradiated diesel fuel.

ADS, as well as the significant effect of supports for TiO_2–CeO_2 on ADS shall be further described in a full article.

For the chemical transformation of organosulfur to sulfone species, active oxygen species are required. It has been reported that organic peroxides can be generated in petroleum by light irradiation via photolysis.[22–24] Aromatic compounds are sensitive to photo-oxidation, in particular those larger and more substituted polyaromatic compounds,[26] that is, 4-ring aromatics tetracene in diesel fuel. Additionally, organic peroxides, that is, cumene hydroperoxide (CHP), were reported to oxidize refractory sulfur compounds to corresponding sulfones in the presence of a catalyst.[27] Therefore, we analyzed the peroxide number of the original and light-irradiated diesel fuel. No peroxide was detected in the original diesel fuel, while it became 12 mmol/kg in the light-irradiated diesel fuel. The result confirmed our hypothesis on peroxides formation during the light irradiation treatment. Based on that, we have also investigated the effect of light source on peroxides generation in the fuel. Figure 3 shows the amount of peroxides generated in the diesel fuel as a function of exposure time under different light sources at an air flow rate of 10 mL/min. Without light, no peroxides were generated even at 100°C. In contrast, peroxides were generated in diesel fuel and increased almost linearly with exposure time by light irradiation under different light sources including mimic sunlight, visible light, as well as room light. The peroxides formation rate (*r*), taking the slope in conc. vs. time curve, follows the order of mimic

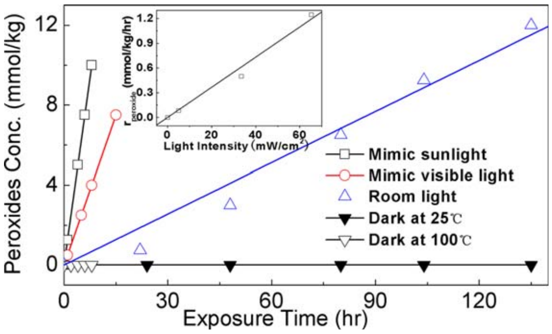

Figure 3. Amount of peroxides (mmol-peroxides/kg) generated in diesel fuel as a function of exposure time under different light sources at 25°C (The inset: the peroxides formation rate as a function of light intensity).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

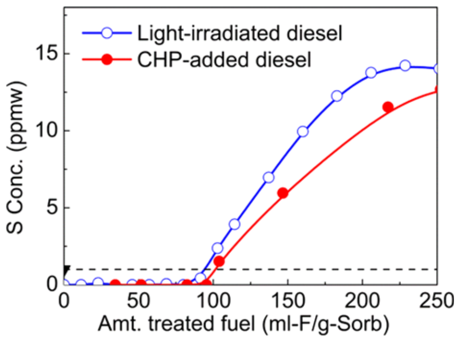

Figure 4. Breakthrough curves of total sulfur compounds over TiO_2–CeO_2/MCM-48 from light-irradiated diesel fuel and cumene hydroperoxide (CHP, 12 mmol/kg) added diesel fuel at 25°C and 9.6 h^{-1} of LHSV.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sunlight > mimic visible light > room light. Given that the measured light intensity was 65.1, 33.5 and 5.0 mW/cm^2 for mimic sunlight, mimic visible light, and room light, respectively, the peroxides formation rate was correlated to the light intensity, as shown in the inset of Figure 3. The linear relationship indicates that peroxides generation in the fuel is strongly dependent on the light intensity applied but insensitive to the photon energy (or wavelength).

To verify the promotion effect of *in situ* generated peroxides via light irradiation on ADS, a model peroxide compound, CHP was added into the original diesel fuel at a concentration of 12 mmol/kg, the same as the peroxide concentration observed in the light-irradiated diesel fuel. The CHP-added diesel fuel was then examined for ADS over the TiO_2–CeO_2/MCM-48 adsorbent under the same conditions. Figure 4 shows the ADS breakthrough curve over the TiO_2–CeO_2/MCM-48 adsorbent from the CHP-added diesel fuel. For comparison, the breakthrough curve obtained from the light-irradiated diesel fuel is also presented. The ADS performance was similar between these two fuels. The breakthrough point was 95 and 101 cm^3-F/g-A or 1.143 and 1.216 mg-S/g-A for the light-irradiated diesel fuel and the CHP-added diesel fuel, respectively. The result supports that organic peroxides generated in diesel fuel by light irradiation did play an important role in ADS over the TiO_2–CeO_2/MCM-48 adsorbent under ambient conditions. It is also noticeable that the adsorption capacity from the light-irradiated diesel fuel was somewhat lower than that from the CHP-added diesel fuel. It may be due to the competitive adsorption over the TiO_2–CeO_2/MCM-48 adsorbent between sulfone species and small amount of by-products, such as phenolic compounds, carboxylic acids, ketones, and alcohols[28] which may be produced from possible side reactions accompanying peroxides generation during light irradiation. It should be mentioned that the *in situ* generated trace amount of organic peroxides in fuel during light irradiation can be harmful due to their health and safety issues, thus proper cautions should be taken when handling the irradiated fuel. Meanwhile, our results indicated that no peroxides were detected after ADS, indicating the peroxides were consumed during ADS, which suggested the ultra-clean fuel can be safe to handle/use. It should also be addressed that the regeneration tests suggested that the TiO_2–CeO_2/MCM-48 adsorbent can be regenerated by the air oxidation.

In summary, a new approach for ultra-deep ADS of diesel fuel was explored, in which the original diesel fuel was first treated by light irradiation followed by selective adsorption over MCM-48 supported TiO_2–CeO_2 mixed oxide adsorbent under ambient conditions. After light irradiation of the commercial diesel fuel, the TiO_2–CeO_2/MCM-48 adsorbent was able to selectively remove refractory sulfur compounds to <1 ppmw with a superior adsorption capacity of 95 cm^3-F/g-A or 1.143 mg-S/g-A, which is over 30 times higher than that for the original commercial diesel fuel. The dramatic promoting effect of light irradiation is probably through *in situ* generation of peroxides in the fuel under both mimic sunlight and visible light. The generated peroxides subsequently transform organosulfurs to sulfone or sulfone-like species, which can be readily adsorbed over the TiO_2–CeO_2/MCM-48 adsorbent.

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