

Ultra-deep Desulfurization of Diesel by Selective Oxidation with Catalysts Assembled in Emulsion Droplets

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Introduction

Much attention has been paid to the deep desulfurization of fuel oils due to more stringent environmental regulations [1]. Oxidative desulfurization (ODS) combined with extraction is considered to be one of the most promising processes and the refractory compounds, such as, 4, 6-dimethyldibenzothiophenes can be oxidized relatively easily under mild reaction conditions. However, the selectivity in these systems is not high enough to oxidize the sulfides present in diesel fuels, and some unsaturated hydrocarbons of the fuel are also oxidized. Furthermore, a large quantity of oxidant is required and the operating cost is increased. To overcome these obstacles, our group developed the emulsion catalysis for the oxidative desulfurization. The efficiency of the emulsion catalyst can be significantly improved because the catalyst is assembled in the surface of the emulsion droplets and therefore can be uniformly distributed in the reaction media (Fig. 1). The emulsion catalyst can be separated and recycled by the demulsification.

This lecture presents the recent development in emulsion catalysis, particularly focuses on the design, synthesis and applications of emulsion catalysts in ultra-deep desulfurization, selective oxidation and asymmetric synthesis. Based on the emulsion catalysis, an ultra-deep desulfurization process for diesel fuel was developed and the sulfur content of diesel is reduced from the several hundred-ppm ranges down to only a few ppms. The emulsion catalysts also show promising performance in selective oxidation and asymmetric synthesis. It is prospected that the emulsion catalysis can provide new opportunities for environmentally benign and green chemistry.

Results and Discussion

The reactivity of different sulfur-containing compounds, such as BT, 5-methylbenzothiophene (5-MBT), DBT, and 4,6-DMDBT (S: 1000 ppm) was investigated for the selective oxidation using $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ as catalyst. The conversions of sulfur-containing compounds versus the reaction time at 30 °C in the emulsion system are shown in Fig 2. The catalytic oxidation reactivity of the sulfur-containing compounds is in the order: $BT < 5-MBT < DBT < 4,6-DMDBT$. Although the oxidation of benzothiophene is relatively difficult due to its low oxidative reactivity, it can be efficiently oxidized in the emulsion system. These results suggest that the sulfur-containing compounds (including dibenzothiophene and its derivatives) present in the pre-hydrotreated diesel can be oxidized completely at room temperature while the sulfur-containing compounds (including benzothiophene, dibenzothiophene and their derivatives) present in the non-hydrotreated diesel can be oxidized at 30 °C.

The oxidative desulfurization process was applied to the desulfurization of actual diesel, such as a pre-hydrotreated diesel and a straight-run diesel. Figs. 3 and 4 show the sulfur-specific gas chromatography (GC) analyses of the original diesel before and after the catalytic

oxidation. The pre-hydrotreated diesel contains a wide range of alkyl-substituted dibenzothiophenes while the straight-run diesel is composed of a wide range of alkyl-substituted benzothiophenes and alkyl-substituted dibenzothiophenes. All sulfur-containing compounds present in the pre-hydrotreated diesel can be oxidized to sulfones at room temperature (22 °C) in 1 h while all sulfur-containing compounds present in the straight-run diesel can be oxidized at 30 °C in 2 h. This suggests that the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ shows a high catalytic activity for sulfur-containing compounds present in the actual diesel.

The sulfones in the oxidized diesel can be removed by a polar extractant, for example, 1-methyl-2-pyrrolidone was used as the extractant to remove the sulfones from the oxidized diesels. The sulfur level of a prehydrotreated diesel can be lowered from 500 to 0.1 ppm after oxidative desulfurization, and that of a straight-run diesel can be lowered from 6000 to 30 ppm after oxidative desulfurization.

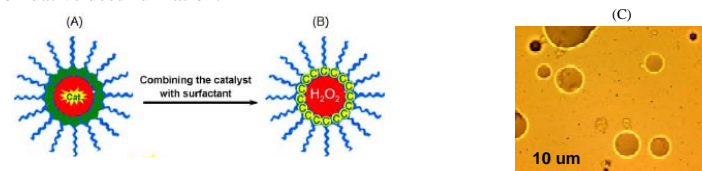


Figure 1. Amphiphilic catalyst assembled in emulsions. (A) The surfactant molecules, assembling in the surface of emulsion droplets, and the catalysts are in the emulsion droplets. (B) Amphiphilic catalyst, assembling in the interface of emulsion droplets instead of only simple surfactant. (C) Optical micrograph of the mixture of the pre-hydrotreated diesel, amphiphilic catalyst, and H_2O_2 .

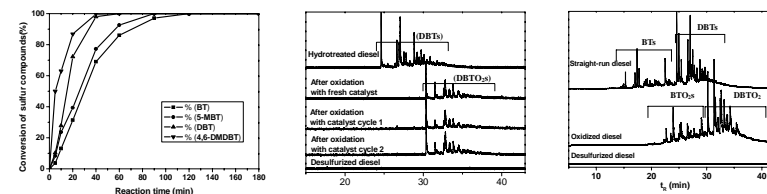


Figure 2. Conversion of sulfur-containing compounds versus the reaction time using emulsion catalysis at 30 °C.

Figure 3. Sulfur-specific GC-FPD chromatograms of the pre-hydrotreated diesel, the pre-hydrotreated diesel after oxidation, and the desulfurized diesel.

Figure 4. Sulfur-specific GC-FPD chromatograms of the straight-run diesel, the straight-run diesel after oxidation, and the desulfurized diesel.

Significance: We successfully accomplished the goal to reduce the amount of sulfur in diesel from its high sulfur content to only a few ppm.

References

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