

Oxidative Desulfurization of Mexican diesel using supported vanadium based catalysts.

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Introduction

Oxidative Desulfurization (ODS) process is considered to be one of the promising new methods for ultra deep desulfurization of fuel oils. It consists on the oxidation of the sulfur compounds to increase their polarity facilitating their extraction [1-4]. The products of S-compounds oxidation are sulfoxides and subsequently sulfones. Several aspects influence the efficiency of this process, which are: oxidant agent, extraction solvent, reaction conditions and catalyst used. Vanadium oxide has demonstrated to improve S-compounds oxidation, thus it has been used as active phase over various supports in our recent studies [5-6]. Then, the aim of this work is to evaluate ODS activity of vanadium-supported catalysts in the ultra deep desulfurization of actual Mexican diesel.

Materials and Methods

Oxidesulfurization of actual Mexican hydrotreated diesel with 350 S-ppm was performed. Hydrogen peroxide was used as oxidant agent, acetonitrile as extraction solvent and vanadium supported on Al_2O_3 , TiO_2 and $\text{Al}_2\text{O}_3\text{-TiO}_2$ as catalysts. Catalysts were characterized by SEM-EDX, XRD, FT-Ramman and TPR. ODS reaction was carried out in a glass batch reactor, equipped with a magnetic stirrer, a thermometer, and a condenser. In a typical run, the solid catalyst was suspended under stirring in a mixture containing diesel, solvent and oxidant at a constant temperature (60°C) and atmospheric pressure.

Results and Discussion

ODS of actual diesel was carried out on these catalysts to study the oxidation reactivity of DBTs compounds prevailing in hydrotreated diesel. During the process, GC-peaks of DBTs almost disappeared (diesel phase) and the peaks of DBT sulfones appeared after oxidation in the solvent phase, indicating that the oxidation of DBTs was leading to the formation of DBT sulfones. These results show that all sulfur-containing compounds can be significantly oxidized to sulfones at 60°C in 30 min. and the main sulfur compound remaining in diesel was 4,6-DMDBT, which is very difficult to be desulfurized. Figure 1 shows a chromatogram of extraction-solvent phase after ODS, there we can observe the extraction of both aromatic compounds and DBTs, and well-defined peaks of DBT sulfone. In this test, we added DBT (450 ppm S) into diesel in order to obtain more evident results.

Figure 2 shows S-specific chromatograms of diesel before and after 30 min. reaction, where we can observe the peak evolution of DBTs, prevailing small amounts of 4-MDBT and 4,6-DMDBT, in contrast DBT was completely removed. Results of the best run indicated that ODS produced desulfurized diesel with S-content as low as 10 ppm, which corresponds to overall S-removal of 99% after 30 min. reaction at 60°C . Then V based catalysts have high catalytic activity for sulfur-compounds present in actual diesel.

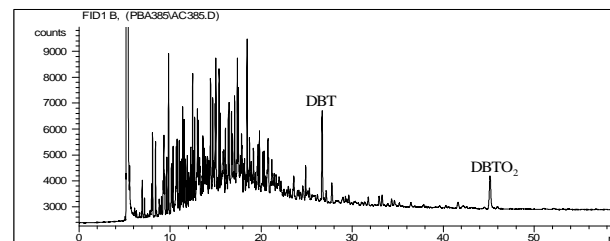


Figure 1. GC-FID chromatogram of solvent phase after ODS of diesel, with additional DBT.

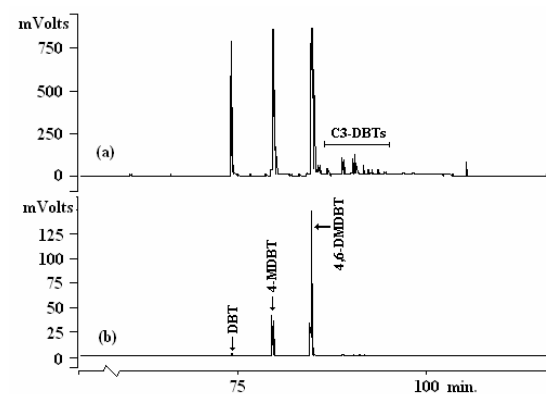


Figure 2. Sulfur specific chromatograms (PFPD) of (a) original and (b) oxidesulfurized diesel. Notice the scales are different.

Significance

ODS process using vanadium based catalysts could be an alternative for ultra deep desulfurization of fuel oil when it is used as HDS post treatment.

References

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