

Oxidative Desulfurization: Catalytic Generation of Organic Hydroperoxide in Refinery Hydrocarbon Streams

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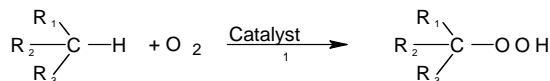
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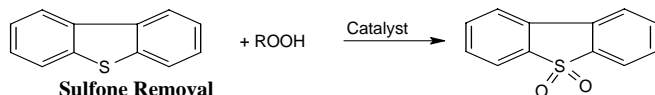
Introduction

Organic hydroperoxides are used as chemical reagents and catalysts and are intermediates in many industrially significant oxidation processes. Organic hydroperoxides are also one component of a novel process for the oxidative desulfurization (ODS) of hydrocarbon streams (Figure 1)¹. The hydroperoxide is used with a catalyst to oxidize refractory organosulfur species to the corresponding sulfones which are then removed by extraction, adsorption or catalytic decomposition. One limitation of the typical ODS process is the use of purchased organic hydroperoxide (i.e., tert. Butylhydroperoxide) as oxidant.

- Alkyl hydroperoxide generation- *In Situ*



- Oxidation of Dibenzothiophenes



- Sulfone Removal

- Adsorption
- Extraction
- Reaction

Figure 1: Three Step Oxidative Desulfurization Scheme

UOP LLC has discovered that organic hydroperoxide can be generated catalytically in high concentration within the refinery stream to be oxidized. This *in situ* generated hydroperoxide can then be used to oxidize the dibenzothiophene derivatives for the ODS process. It is known from the literature that homogeneous transition metal salts can be used to catalyze the autoxidation of hydrocarbons. We have found heterogeneous catalysts can also be employed, with obvious process advantages, to oxidize a variety of diesel feedstocks to give organic hydroperoxide products containing more than 2 wt% hydrogen peroxide equivalent.

Materials and Methods

A variety of commercial and laboratory prepared diesel range feedstocks have been oxidized. Mild hydrotreating of all feeds was conducted to achieve 100-700 ppm sulfur. Catalyst synthesis and characterization has been documented.²

Oxidation experiments were conducted in a batch mode using high pressure stirred autoclave reactors. In a typical experiment the feedstock and catalyst were loaded into the autoclave and the reactor was sealed. The reactors were pressurized with 8% O₂/92% N₂ and then the reactor contents were heated to the target temperature. After a set amount of time the liquid products were sampled and submitted for peroxide analysis, total oxygen analysis and other characterization as appropriate.

Results and Discussion

The objective in designing a heterogeneous catalyst for hydroperoxide formation was to catalyze autoxidation at milder conditions.³ A variety of catalysts were prepared. A formulation containing manganese on magnesium oxide support was clearly superior for peroxide generation in diesel feed. The optimum catalyst was found to contain a particular mixed metal oxide phase – Mg₆MnO₈.

Diesel feedstocks of varying composition were successfully oxidized (Figure 2) to levels sufficient for diesel ODS. Catalyst, process and feedstock variables have been studied and various aspects of this work will be presented.

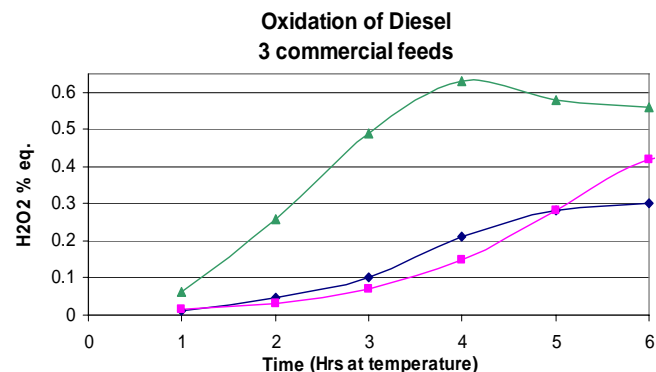


Figure 2. Catalytic Generation of Organic Hydroperoxide with Three Feedstocks.

Significance

In situ generation of alkylhydroperoxide is a key component of an oxidative reaction scheme which may provide an alternate to deep hydrotreating for desulfurization of refinery hydrocarbon streams.

References

- a. US Patent 6277271, Kocal, J. A. inventor. (assignee, UOP LLC) b. US Patent 6368495 Kocal, J. A.; Brandvold, T. A. inventors. (assignee, UOP LLC)
- US Patent 7038090, Brandvold, T. A.; Lewis, G. L.; King, L. M.; Brewer, L. E., inventors (assignee, UOP LLC)
- Sheldon, R. A.; Kochi, J. K. *Advances in Catalysis*, **1976**, 25 272-413.