ADVANCED OXIDATION PROCESS

Final Report

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DISCLAIMER

ABSTRACT

The removal of recalcitrant sulfur species, dibenzothiophene and its derivatives, from automotive fuels is an integral component in the development of cleaner burning and more efficient automobile engines. Oxidative desulfurization (ODS) wherein the dibenzothiophene derivative is converted to its corresponding sulfoxide and sulfone is an attractive approach to sulfur removal because the oxidized species are easily extracted or precipitated and filtered from the hydrocarbon phase. Fe-TAML® activators of hydrogen peroxide (TAML is Tetra-Amido-Macrocyclic-Ligand) catalytically convert dibenzothiophene and its derivatives rapidly and effectively at moderate temperatures (50-60 °C) and ambient pressure to the corresponding sulfoxides and sulfones. The oxidation process can be performed in both aqueous systems containing alcohols such as methanol, ethanol, or t-butanol, and in a two-phase hydrocarbon/aqueous system containing *tert*-butanol or acetonitrile. In the biphasic system, essentially complete conversion of the DBT to its oxidized products can be achieved using slightly longer reaction times than in homogeneous solution. Among the key features of the technology are the mild reaction conditions, the very high selectivity where no over oxidation of the sulfur compounds occurs, the near stoichiometric use of hydrogen peroxide, the apparent lack of degradation of sensitive fuel components, and the ease of separation of oxidized products.

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A PORTION OF THIS PRESENTATION WAS GIVEN IN A FINAL REPORT TO PARSONS INFRASTRUCTURE AND TECHNOLOGY GROUP, P.O. BOX 61, SOUTH PARK, PA 15219 (PARSONS TASK NO. 734931) FOR SUPPORT OF THE INSTITUTE TO STUDY AN OXIDATIVE DESULFURIZATION TECHNOLOGY BASED ON TAML ACTIVATORS OF HYDROGEN PEROXIDE

INTRODUCTION

Technical Discussion: Background

The USEPA developed a regulatory plan for the petroleum industry targeted at lowering sulfur levels in gasoline and diesel fuels.[1-3] This will require the engine manufactures to design and build better engines and the petroleum industry to supply fuels substantially free of sulfur compounds.[4,5] The petroleum industry needs to find and implement a desulfurization technology soon.[6-9] The future lies in the development of innovative technologies for removing the traces of sulfur compounds present after applying the standard hydrodesulfurization technology. This report describes the advances achieved by the Institute for Green Oxidation Chemistry (Institute) at Carnegie Mellon University in the area of oxidative desulfurization (ODS) using TAML® activators of H_2O_2 while supported under **DOE Award No. DE-FC26-02NT41625** for the period September 26, 2003 – September 25, 2003.

Description of the TAML® Activator/H_2O_2 Technology

TAML® activators (**T**etra**A**mido **M**acrocyclic **L**igand) are a structurally and chemically unique class of H_2O_2 activators **Figure 1**.[10-12]

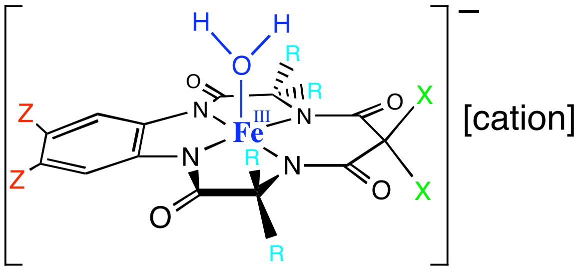


Figure 1: TAML activator showing potential substituent sites.

Catalyst features that are relevant to an ODS process include the following:

- the modular synthesis used to prepare the activators has allowed for the synthesis of 20 unique molecules thus far
- flexibility in choosing the cation makes them soluble in organic or aqueous media
- they are effective at low concentrations (0.1–5 ppm)

- their reactivity can be controlled
- they use peroxide efficiently

The catalysts can be used to oxidize dibenzothiophene (DBT) derivatives at moderate temperatures and at ambient pressure using hydrogen peroxide. The chemistry can be carried out under single or two-phase reaction conditions. Under two-phase conditions, an inverse phase transfer catalysis scenario apparently exists which facilitates reaction of the hydrocarbon soluble dibenzothiophene with the aqueous TAML/ H_2O_2 system.

Summary of Initial Desulfurization Studies using TAML Activators

Figure 2 shows dibenzothiophene (DBT) and benzothiophene (BT) derivatives that were rapidly oxidized by H_2O_2 in the presence of the TAML activator $FeBF_2$ (X= F, Z = H, and R = CH_3). These results preceded current support. When the oxidation was carried out in a 70:30 water/*tert*-butanol mixture the corresponding sulfone was formed exclusively. The *tert*-butanol (t-BuOH) solubilizes DBT and BT derivatives in water. DBT, 4-MDBT, and 4,6-DMDBT are the compounds of prime interest for an ODS process because they are the predominant sulfur species remaining after hydrodesulfurization.

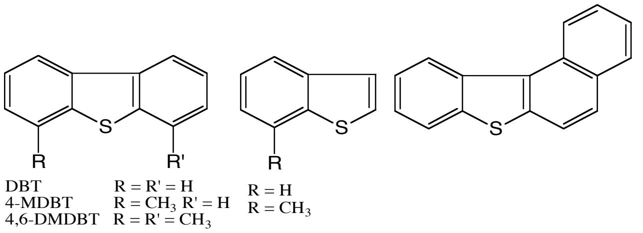


Figure 2: The benzothiophene compounds examined

Previous studies with the $FeBF_2$ TAML activator revealed that DBT oxidation could be achieved in less than 5 min using a 1:500 TAML:DBT ratio on a molar basis in water containing 30% t-BuOH, 60 °C, pH 7 with KH_2PO_4 buffer, and atmospheric pressure. Even when molar ratios of substrate to catalyst ranged from approximately 2000:1 to 7000:1 reactions were done within one hour (T = 60 °C).

TARGETS

The principle efforts in the Institute during the funding period have been directed toward

- examining different TAML activators for DBT oxidation
- determining reactivity toward essential fuel components
- determining the efficiency of the reaction
- examining diesel mimics

- exploring the role that reaction medium has on the oxidation process

Investigations in the final area are of particular significance as the move toward practical application of the TAML/H_2O_2 technology is contemplated.

EXPERIMENTAL

ANALYTICAL METHODS: used to characterize compound identities included UV-vis, IR, NMR spectroscopies, GC-MS and GC-AED and combustion analysis.

Sample Experimental Procedure for Single Phase Reactions: To a stirred H_2O:t-BuOH (7:3) solution of DBT (1.3×10^{-3} M) at 60^0 C was added the Fe-TAML activator and H_2O_2. The reaction mixture was stirred for 30 min. then the t-BuOH was removed in vacuo and the water layer extracted with diethyl ether. A GC-MS of the ether solution was obtained.

Sample Experimental Procedure for BiPhasic Reactions:A two-phase system consisting of 5 mL of H_2O:t-BuOH (7:3) 1 mL of DBT (3.4×10^{-3} M) was prepared. The mixture was heated to 60 °C and then Fe-TAML activator (1.4 μM) and H_2O_2 (54 mM) were added. The reaction mixture was stirred for 1 h. Then a second portion of Fe-TAML activator (1.4 μM) and H_2O_2 (54 mM) was added. Total reaction time was 2 h. The n-Octane layer was separated from the aqueous phase. The t-BuOH was removed in vacuo and the water extracted with diethyl ether. Both the ether extract and n-Octane layers were analyzed by GC-MS.

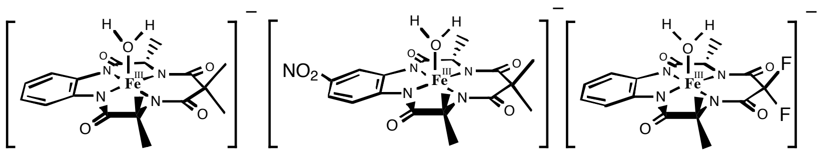
SUMMARY OF RESULTS

- **TAML catalysts** – determined that the prototype TAML catalyst could oxidize in a stepwise process the DBT under slightly modified conditions compared to the most reactive catalyst
- **Fuel Integrity** – determined that under standard reaction conditions with the most reactive TAML catalyst no hydrocarbon oxidation occurred
- **Peroxide Efficiency** – determined that nearly complete conversion of DBT to its sulfoxide and sulfone resulted when using stoichiometric amounts of H_2O_2 relative to DBT
- **Diesel Mimics** – determined that the oxidation of DBT was readily achieved in bi-phasic systems provided an agent was present that could transfer the DBT into the aqueous phase where oxidation by the TAML activator could occur
- **Effect of Reaction Medium** – determined that the oxidation of DBT was strongly dependent on reaction medium
    - the presence of hydrocarbons in water resulted in slower reactions and a higher degree of formation of the singly oxidized form of DBT
    - the amount and type of co-solvent affects the degree of DBT oxidation and its rate

RESULTS AND DISCUSSION

TAML catalyst

The three TAML activators shown in **Figure 3** were used in this investigation. $FeBF_2$ is the most active TAML activator while FeB* (X= CH_3, Z = H, and R = CH_3) is the least active. The vast majority of the studies utilize $FeBF_2$ because it is sets the standard for reaction in terms of rate, substrate specificity, and oxidizing strength or, in negative terms, it could have the highest propensity to damage hydrocarbons present in the fuels. However, FeB* is currently undergoing scale-up synthesis to metric tonne quantities. Thus, if this catalyst were suitable for DBT oxidation, the time to implementing a commercial ODS process involving TAML activator/peroxide technology would be greatly shortened.



FeB*

$FeNO_2B$*

$FeBF_2$

Figure 3: TAML oxidant activators used for the DBT oxidation

As described above, DBT derivatives oxidized using $FeBF_2$ in a water/t-BuOH mixtures produced only the sulfone. This changes when either $FeNO_2B$* (X= CH_3, Z = H, NO_2, and R = CH_3) or FeB* are used. A reaction performed using $FeNO_2B$* and H_2O_2 produces both the sulfone and sulfoxide forms of DBT and the reaction is slower compared to $FeBF_2$. **Figure 4** is the GC trace showing residual DBT and the two oxidation products in nearly equal concentration. This result clearly demonstrates the stepwise conversion process expected, but not proven, with the $FeBF_2$ catalyst. Conversion of the DBT to either oxidized product is sufficient to significantly enhance extractability into polar phases from a hydrocarbon mixture. We are in the process of determining the relative rates of reaction of the DBT to its sulfoxide and the corresponding sulfoxide to its sulfone with the TAML/H_2O_2 system.

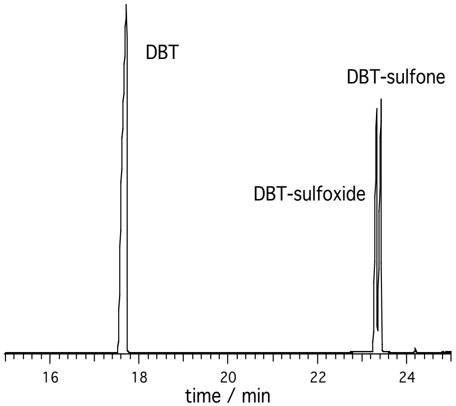


Figure 4: GC trace of aqueous phase after oxidation using $FeNO_2B$*

When the FeB* catalysts is used, a result similar to that for the $FeNO_2B^*$ activator is obtained. For FeB*, pH 10 KH_2PO_4 buffer is used rather than pH 7 KH_2PO_4 buffer. The FeB* TAML activator is significantly more reactive at pH 10 than pH 7. The GC trace for one of these experiments is shown in **Figure 5**, reaction conditions: DBT (8.22×10^{-4} M, 150 ppm) FeB* (8.22×10^{-6} M, 3.6 ppm), and H_2O_2 (3.3×10^{-2} M), 0.01 M pH 10 phosphate buffer:t-BuOH (7:3), T = 100 °C, t = 1 h. Approximately 90% of the DBT was oxidized within 1 hr. The ability to use the FeB*, the simplest TAML activator, is significant because it is undergoing scale-up to industrial levels. We believe that this has significantly shortened the path to commercial adoption of a TAML activator based oxidative desulfurization process.

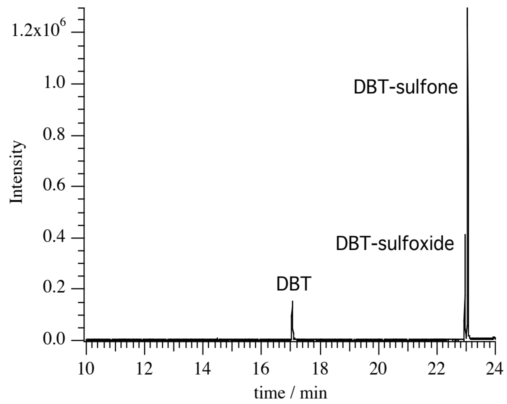
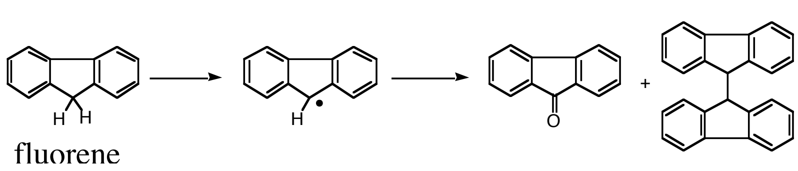


Figure 5: GC trace of aqueous phase after oxidation using FeB*

Fuel Integrity

Hydrogen peroxide can generate the hydroxyl radical under a wide variety of reaction conditions. This radical is capable of degrading hydrocarbons in the fuel. To check the selectivity of the TAML/H_2O_2 chemical oxidation process, fluorene, Eq. 1, was chosen as a model hydrocarbon because of its structural similarity to DBT and it has C-H bonds that are susceptible to radical reactions. The C-H bond of the methylene carbon has a bond strength of 74 kcal/mol. A GC/MS analysis of this reaction following typical reaction conditions for the $FeBF_2$ catalyst showed fluorene as the only observable product. Thus the predominant oxidant generated by the TAML/H_2O_2 system does not perform H-atom abstraction chemistry under the reaction conditions used for DBT oxidation.

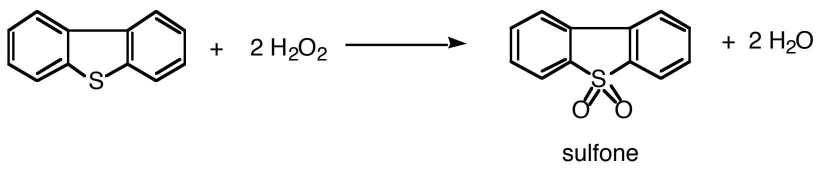


Eq. 1

A second check for potential oxidation of fuel components was done using toluene. Typical reaction conditions for the $FeBF_2$ catalyst were applied. No toluene oxidation was observed by GC analysis. Thus the TAML activator/H_2O_2 system is reactive enough to rapidly oxidize the sulfur components in fuel without degrading the hydrocarbons.

Efficiency of Peroxide Usage

A key component in adopting the TAML activator technology for fuel desulfurization is efficient peroxide use. The stoichiometric reaction for conversion of DBT to its sulfone is given in Eq. 2. Thus a reaction was performed with a 1:2 DBT:H_2O_2 stoichiometry. The DBT:TAML activator ($FeBF_2$) ratio was 1000:1. After one hour of reaction >95% of the DBT was converted to the corresponding sulfoxide and sulfone as determined by GC, **Figure 6**. The majority product is the sulfone. Thus H_2O_2 is used efficiently by even the most reactive TAML activator. It is noteworthy that at such low catalyst and hydrogen peroxide concentrations, (1.73 μM) and (3.46 mM), respectively, that nearly 1000 turnovers of substrate occurred in such a short amount of time. Since both DBT oxidation products can be extracted from the hydrocarbon phase, it might be possible that conditions can be found where only one equivalent of H_2O_2 will be necessary for the successful application of this chemistry. This would make it even more advantageous over the other ODS technologies where large excesses of H_2O_2 relative to DBT are used .



Eq. 2

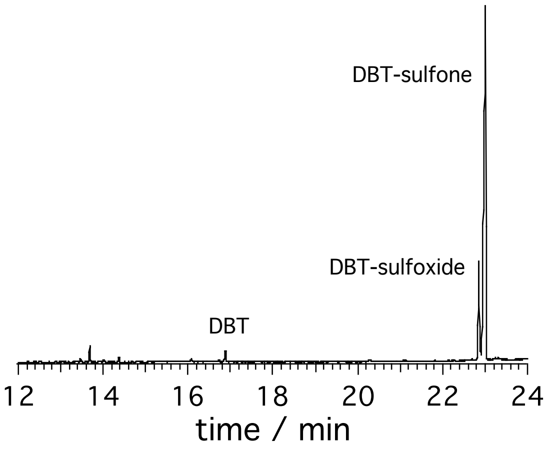


Figure 6: GC trace of $FeBF_2$ catalyzed oxidation of DBT using a 2:1 H_2O_2:DBT stoichiometry.

Diesel Mimics

It had been proposed to study reactions where DBT was dissolved in a hydrocarbon while the TAML activator was in the aqueous phase. It was conjectured that if the reaction could be performed in a two phase system then the TAML activator and any excess peroxide could be separated from the hydrocarbon by standard phase separation techniques once the oxidation reaction was completed and the hydrocarbon taken on for further processing. However, it was not apparent how the DBT could be drawn into the aqueous phase for oxidation by the TAML activator/H_2O_2 system nor once oxidized what the partitioning of the product(s) between the hydrocarbon and aqueous phases would be. Competing ODS technologies rely on an extraction step to remove the oxidized DBT's.[13-18]

The best results for the aqueous based chemistry were obtained when t-BuOH was present at 30% relative to water, so it was included at least at this level in all subsequent studies. For the experiments described below, the DBT was dissolved in n-octane and this is layered onto the water/t-BuOH. The two-phases are then heated and stirred vigorously creating what appears to be an emulsion. Shown in **Figure 7** is the GC trace of the water/t-BuOH layer obtained after 2 hr; reaction conditions: DBT (3.4×10^{-3} M, 890 ppm) in octane, $FeBF_2$ TAML activator (2.8 μM) and H_2O_2 (0.1 M), T = 60 °C, t = 2 h. The GC trace reveals substantial DBT conversion and two products are formed. It is clear from this experiment that a biphasic system is viable route for the removal of DBT compounds from hydrocarbons.

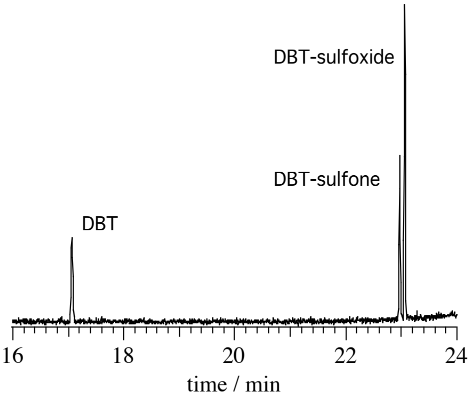


Figure 7: GC trace of the water/t-BuOH layer 2 hr reaction. $FeBF_2$ activator.

While lower DBT conversion rates were anticipated because of either the need to extract the DBT from the octane into the aqueous phase or reaction at the water/hydrocarbon interface, appearance of the DBT-sulfoxide was unexpected with the $FeBF_2$ catalyst. It is possible that small amounts of hydrocarbon also transfer into the aqueous phase modifying the micro-environment around the TAML activator or DBT/DBT-sulfoxide[19-21] resulting in the observed stepwise process. This behavior was also observed when water soluble hydrocarbons were added to the aqueous phase (see below). The DBT detected in **Figure 7** is artifactual. Subsequent experiments did not show DBT in the water/t-BuOH phase at least at room temperature. ^{1}H NMR experiments are in progress to determine if the DBT is extracted at least in part into the water/t-BuOH during reaction.

The GC trace of the octane layer is shown in **Figure 8** (reaction conditions like those in **Figure 7**). As expected, there is unreacted DBT, but no oxidation products are observed. One challenge for the ODS approach has been finding methods for extracting the oxidized products from the hydrocarbon phase. With the TAML activators in the water/t-BuOH mixture this appears not to be a problem. It seems that as the DBT is extracted into the water/t-BuOH phase it is oxidized and the products retained.

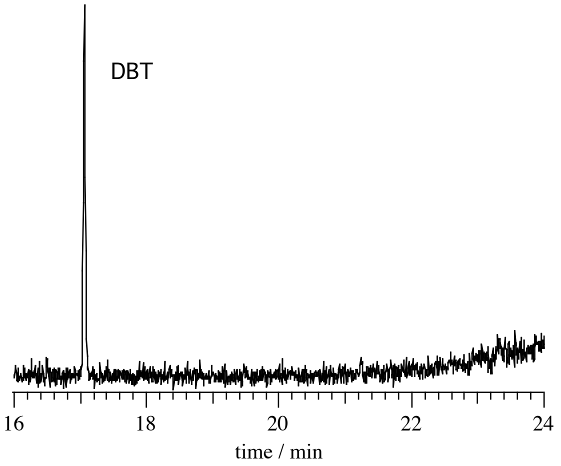


Figure 8: GC trace of the octane layer after 2 hr reaction using $FeBF_2$ TAML activator and H_2O_2.

The reaction with FeB* also resulted in conversion of DBT to its corresponding sulfone and sulfoxide at pH 10, T = 100 °C and 3 h reaction. Although the conversion was only modest, >10%, no efforts were made to maximize the oxidation rate. The lower conversion compared to $FeBF_2$ was expected given the generally lower reactivity of FeB* compared to $FeBF_2$. Furthermore, it appears as though a portion of the t-BuOH might be azeotroping out of the reaction mixture thereby effectively lowering its concentration. A pressurized reactor is needed for future studies. Interestingly, the same extent of reaction with FeB* catalyst could be achieved by heating to only 40 °C but with the application of ultrasound from a standard laboratory sonicator. Investigation of whether this is due to local heating or some other phenomenon is an ongoing.

Effect of Reaction Medium

A greater degree of DBT conversion was obtained when more t-BuOH was added to the water. With a 1:1 H_2O:t-BuOH mixture, the degree of conversion increases to more than 85% under the otherwise same reaction conditions as in **Figure 7**. This behavior is likely due to a greater availability of t-BuOH in both phases at the higher concentration. However, it did not appear to be possible to exceed the 85% conversion with t-BuOH even though a variety, but not exhaustive set of reaction conditions were explored. Methanol and ethanol were also examined briefly as extracting agents. The advantage of using these alcohols is that their extremely low solubility in hydrocarbons which could lessen processing after reaction. With both alcohols, the DBT sulfoxide and DBT sulfone were detected in the aqueous phase and the degree of DBT conversion was lower for the same amount of reaction time. In the case of t-BuOH, a number of different ratios of t-BuOH to water were explored before finding the optimum one of 7:3 H_2O/t-BuOH. Thus it might be that with further exploration of reaction conditions with MeOH and EtOH, better conversion can be found. Nevertheless, the differences found with the alcohols demonstrates that reaction medium will play a significant role in this chemistry.

Upon changing the extracting agent to acetonitrile (CH_3CN) and using 50°C rather than 60 °C, essentially 100% conversion of the DBT was possible. Furthermore, the reaction appears to be faster using CH_3CN than t-BuOH. The faster reaction is somewhat surprising since CH_3CN has essentially no solubility in hydrocarbons and thus it might be expected to be less effective for this reaction. This result suggests that the inverse phase transfer catalysis notion that we were basing the t-BuOH results upon may not be correct. Acetonitrile is one of the solvents that has been suggested as a means for extracting DBT sulfones and sulfoxides from diesel fuels. We are continuing to look at the use of CH_3CN as the ternary agent by moving to actual diesel samples. This has awaited the arrival of a new instrument that could detect low concentrations of sulfur species in the presence of high hydrocarbon concentrations.

It was also of interest to determine if the DBT oxidation chemistry was modified by the presence of other hydrocarbons that might extract into the water/t-BuOH phase. Thus an experiment was performed in which fluorene (1.05×10^{-3} M, 175 ppm) was added to a water/t-BuOH mixture containing $FeBF_2$ (1.2 μM) and DBT (1.19×10^{-3} M, 220 ppm); H_2O_2 (0.05 M), T = 60 °C, t = 30 min. The GC trace of the reaction mixture showed unmodified fluorene, but surprisingly DBT conversion was incomplete and both oxidized products were observed. Interestingly, the sulfoxide was the predominant product whereas it is the sulfone that is typically the more abundant. This result is analogous to what was detailed above for the two-phase oxidation chemistry. We are attempting to determine how the presence of even a small amount of a hydrocarbon that does not participate in the reaction can influence the reaction chemistry to such a degree.

Conclusion

The removal of recalcitrant sulfur compounds from diesel and gasoline requires the development of new technologies. We have found that a variety of TAML activators can be used to smoothly oxidize these recalcitrant compounds under a wide range of reaction conditions. Furthermore, since the oxidation process is selective for the sulfur compounds over hydrocarbons in the fuel and the process is efficient in terms of hydrogen peroxide usage, it is very competitive with other ODS approaches. The chemistry is versatile in that it can be performed under both single- and bi-phasic reaction conditions with many choices in how to actually achieve the oxidation. The robustness of reaction clearly is an important factor in the future development of the TAML activators for fuel desulfurization.

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