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Catalytic Oxidative Desulfurization of Diesel Fuels Using Air in a Two-Step Approach

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ABSTRACT: This study presents a novel approach to fuel desulfurization in two steps where air is used as oxidant for the in situ generation of hydroperoxides from aromatics in diesel fuel and then the sulfur compounds are oxidized by the hydroperoxides to sulfones. Bulk and supported CuO based catalysts were examined for oxidation of surrogate and real diesel fuels for generation of hydroperoxides in situ using air. Among bulk CuO, CuO/Al_2O_3, CuO/SiO_2, CuO/TiO_2, and $CuO\text{-}ZnO/Al_2O_3$ tested, CuO/Al_2O_3 gave the highest conversion, but the highest yield and selectivity for hydroperoxide was obtained on bulk CuO catalyst for liquid phase air oxidation of isopropylbenzene. H_2-Temperature programmed reduction (H_2-TPR) revealed the presence of dispersed CuO phase on supported catalysts with bulk CuO as the dominant phase on the unsupported catalyst. Three real diesel fuels were tested for liquid phase air oxidation at 120 °C in the presence of bulk CuO catalyst which revealed different levels of hydroperoxides generation. This was consistent with model aromatic compound study which showed different levels of hydroperoxide formation in the order of isopropylbenzene > cyclohexylbenzene ≈ *sec*-butylbenzene ≫ isopropylnaphthalene. As the second step of the process, the hydroperoxides formed in the real diesel fuel were then tested as oxidant for oxidation of sulfur compounds over Al_2O_3 and SiO_2 supported MoO_3 catalysts. MoO_3/SiO_2 catalyst was more effective with higher activity and selectivity for oxidation of 4,6-dimethyldibenzothiophene in diesel fuel with a total S concentration of 41 ppmw. At 40 °C, 90% of sulfur compounds in diesel were oxidized at oxidant to sulfur molar ratio of 25. Selectivity ((% of sulfone produced)/(% of peroxide consumed)) measurement revealed 82% selectivity over MoO_3/SiO_2 catalyst and only 43% over MoO_3/Al_2O_3 catalyst under similar conditions. Catalysts with varying MoO_3 loadings on both supports were characterized by XRD and H_2-TPR methods. The results show that MoO_3 based catalysts which have a weak interaction with the support might be more preferred for sulfur oxidation.

1. INTRODUCTION

Strict sulfur regulations for diesel fuel mandated in the United States and European Union in the past decade enabled successful implementation of <15 ppm sulfur diesel fuel in these regions.[1,2] Although this was marked by improvements in hydrodesulfurization (HDS) catalysts along with use of high severity conditions, there was considerable interest to employ oxidative desulfurization (ODS) as a finishing process to meet the sulfur specifications.[3] High oxidation reactivity for alkylated dibenzothiophenes even at ambient temperature and pressure rendered ODS as a favorable alternative, eliminating the need for severe conditions required to remove these compounds by conventional HDS.[1−3] Various oxidants (hydrogen peroxide,[4] ozone,[5] nitrous oxide,[6] and *tert*-butyl hydroperoxide[7,8]) in the presence of catalysts were shown to be effective for oxidation of alkylated dibenzothiophenes. But the high cost, storage, and handling issues of peroxide based oxidants rendered these systems unfavorable.[9] With the rest of the world adopting low sulfur and ultra low sulfur diesel in the coming years,[10] there is still a considerable widespread interest in developing cost-effective ODS systems.[11−13]

In an effort to realize the use of cheaper oxidants for ODS, some earlier studies have focused on using air as an oxidant. For example, Nomura and co-workers proposed the use of air and Co salts as catalyst in the presence of sacrificial aldehyde as reagent.[14] This enabled in situ generation of peroxy acids for selective oxidation of dibenzothiophenic type sulfur compounds to corresponding sulfones. In another study, supported cobalt based catalysts were shown to be effective toward air oxidation of sulfur compounds in real diesel fuel to sulfones at temperatures between 120 and 180 °C.[15] But selectivity of one-step air based oxidation toward sulfur and aromatic compounds was not investigated or discussed.

In order to develop a reagent-free process with high selectivity for oxidation of sulfur compounds using air as an oxidant, our laboratory has been investigating a two-step catalytic process using air as an oxidant.[16] In the first step, alkyl aromatic types of compounds present in distillate fuels are air oxidized to alkyl aromatic hydroperoxides which then are used as oxidant in the second step for selective oxidation of sulfur compounds. The scheme of the two-step oxidation process based on air with substituted alkyl benzene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) as representative aromatic and sulfur compounds is presented as Figure 1. By utilizing this two-step catalytic oxidation approach in combination with adsorption of oxidized sulfur compounds, sulfur concentration of a real low sulfur diesel was reduced from 41 to 8 ppmw S.[16]

The present study focuses on the effects of supported and bulk catalysts on the two steps of the air based catalytic

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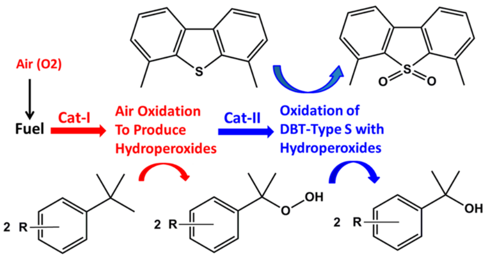

Figure 1. Scheme of two-step oxidative desulfurization process using air as an oxidant with an substituted alkylated benzene and 4,6-DMDBT as representative aromatic and sulfur compounds, respectively, in diesel fuel.

oxidation process. While our previous work showed that unsupported CuO catalyst was effective in air oxidation of real diesel fuel to generate hydroperoxides in situ, this work presents a more detailed investigation of liquid phase air oxidation of model fuel over a series of CuO based catalysts, viz., unsupported CuO, supported catalysts prepared by wet-impregnation procedure $10CuO/Al_2O_3$, $10CuO/SiO_2$, and $10CuO/TiO_2$ and a commercially obtained $CuO{-}ZnO/Al_2O_3$ catalyst. Catalyst characterization by Brunauer−Emmett−Teller (BET) and H_2-temperature programmed reduction (H_2-TPR) methods is also reported. Both surrogate fuel containing different types of alkyl aromatics and three real diesel fuels, LSD_350, LSD_41 and ULSD_15 obtained from BP America were investigated for catalytic air oxidation to generate hydroperoxides. The efficacy of hydroperoxides generated in situ as oxidants for selective oxidation of sulfur compounds in real diesel fuel was examined over both MoO_3/SiO_2 and MoO_3/Al_2O_3 catalysts prepared by wet-impregnation procedure with varying molybdenum loadings and were characterized by H_2-TPR and powder X-ray diffraction (XRD) techniques.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. For air oxidation, supported CuO based catalysts were prepared by wet impregnation of aqueous copper nitrate hemipentahydrate on γ-Al_2O_3 (UOP LaRoche VGL-15), TiO_2, and fumed SiO_2 (Cabosil M5) supports. Impregnated supports were then dried at 80 °C in an oven overnight before being subjected to calcination. Bulk CuO was obtained by direct calcination of copper nitrate hemipentahydrate. A commercial catalyst $CuO{-}ZnO/Al_2O_3$ (MDC-3 from Sud-Chemie) was also tested for air oxidation experiments. All catalysts were calcined at 450 °C for 5 h prior to testing.

For sulfur oxidation of fuel, catalysts were prepared by wet impregnation of ammonium molybdate tetrahydrate on γ-Al_2O_3 (UOP LaRoche VGL-15) and fumed SiO_2 (Cabosil M5) supports. Impregnated catalysts were then calcined at 550 °C for 5 h.

2.2. X-ray Diffraction. Powder X-ray diffraction patterns of the calcined catalysts were obtained on a Scintag (Thermo Scientific) PAD V powder diffractometer using Cu Kα radiation ($l = 0.154$ nm) operated at 30 mA and 35 kV with a scanning speed of 1 deg/min following Joint Committee on Powder Diffraction Standards (JCPDS). The diffractograms were analyzed using MDI JADE 8.0 software and the standard JCPDS files.

2.3. BET Surface Area. N_2 adsorption−desorption was carried out at liquid-N_2 temperature (−196 °C) to measure the BET surface area and pore volume on a Micromeritics ASAP 2020 analyzer. Each sample was degassed by heating at 150 °C under vacuum prior to the measurement and standard test method for measuring the surface area of catalyst and catalyst carriers was applied (ASTM D3663).

2.4. H_2 - Temperature Programmed Reduction. H_2-TPR was carried out from 50 to 900 °C using freshly calcined catalyst samples on a Micromeritics AutoChem 2910 TPR/TPD analyzer. Prior to analysis, catalysts were pretreated at 200 °C for 60 min by passing helium stream. H_2-TPR runs were carried out at a heating rate of 10 °C/min in a flow of 5% H_2 in argon. H_2 consumption was measured by a thermal conductivity detector (TCD).

2.5. Peroxide Number by Iodometric Titration. The peroxide number of the fuel was estimated by iodometric titration based on the procedure outlined in ASTM-D 3707-99 (standard test method for peroxide number of aviation turbine fuels). Briefly, peroxide-containing fuel dissolved in carbon tetrachloride is contacted with aqueous potassium iodide solution. The peroxides present in the fuel are reduced by potassium iodide. An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution. The results were calculated as milligrams per kilogram (mg/kg) of peroxide.

$$\text{peroxide number (PN, mg/kg)} = [(A - B)N \times 1000 \times 8]/S$$

where: A = milliliters of $Na_2S_2O_3$ solution required for titration of the sample, B = milliliters of $Na_2S_2O_3$ solution required for titration of the blank, N = 0.01 N $Na_2S_2O_3$ solution, and S = grams of the sample used.

In a typical experiment, a known amount of fuel containing peroxide was taken in a 250 mL iodine flask that was flushed with nitrogen to remove any dissolved oxygen present in the fuel. Carbon tetrachloride (25 mL) was added to the sample, and a vigorous flow of nitrogen was passed through the solvent for 1 min. Without stopping the gas flow, 20 mL of acetic acid was added to the solution and the gas flow rate was reduced so that the rate was approximately 1 bubble/s. Then a solution of KI (2.4 g of KI in 2 g of distilled water) was added dropwise, and the solution was mixed vigorously for 30 s. The flask was then allowed to stand for 5 min. At the end of the reaction, 100 mL of distilled water was added and the flow of nitrogen gas was stopped. Starch solution (5 mL) was added and was titrated against 0.01 N $Na_2S_2O_3$ solution to the disappearance of blue color.

2.6. Estimation of Oxidation of Sulfur Compounds. To estimate the percentage of sulfur compounds oxidized by peroxides generated in situ, the oxidized fuel containing sulfoxides and sulfones were treated with silica gel (Davisil, grade 635; pore size, 60 Å; 60−100 mesh from Sigma Aldrich). This enables almost complete removal of oxidized sulfur compounds from the liquid fuel. In a typical experiment, 3 g of diesel fuel containing oxidized sulfur compounds was treated with 0.3 g of silica gel sorbent at atmospheric pressure and 30 °C for 30 min. The fuel after adsorption was free of oxidized sulfur compounds. Total sulfur concentration of the treated or adsorbed fuel represents the concentration of sulfur compounds not oxidized, from which percentage of sulfur compounds oxidized in diesel fuels was calculated.

The total sulfur concentration in real fuel was analyzed by using an Antek 9000 series total sulfur analyzer. Qualitative analysis of the sulfur compounds in real fuel was conducted with HP 5890 gas chromatograph (XTI-5 column from Restek; 30 m in length and 0.25 mm in internal diameter) equipped with a pulsed flame photometric detector (PFPD).

Table 1. Physical Properties and Oxidation Activities of Supported and Bulk CuO Based Catalysts for IPB Oxidation[a]

catalyst	surface area, m^2/g	pore vol, g/cm^3	IPB conv., wt %	IPB hydroperoxide yield, wt %	hydroperoxide selectivity, %
none			3.4	3.9	92.2
$10CuO/SiO_2$	219.4	1.62	0.6	0.6	81.1
$10CuO/TiO_2$	37.6	0.33	3.0	1.6	41.7
$10CuO/Al_2O_3$	159.7	0.99	20.3	7.4	29.0
$CuO-ZnO/Al_2O_3$	58.6	0.21	16.4	9.0	43.5
CuO	0.7	0	9.3	9.5	80.6

[a] Reaction conditions: 40 g of isopropylbenzene (IPB); 0.4 g of catalyst; temperature, 120 °C; air flow rate, 220 mL/min.

2.7. Reaction Procedure. For air oxidation reaction, a 200 mL three-necked round-bottom flask fitted with a condenser, stirrer, and an air sparger was charged with hydrocarbon and catalyst. The reaction temperature was maintained at 120 °C, and reaction pressure was atmospheric. The air flow rate was maintained at 220 mL/min. Approximately 0.6 g of sample was collected every hour and was analyzed by gas chromatography—flame ionization detector (GC-FID) and iodometric titration. Model compounds used for air oxidation studies were obtained from Sigma Aldrich and were used as is without any purification. Three real diesel fuels LSD_350, LSD_41, and ULSD_15 obtained from BP America were also tested for air oxidation studies. LSD_350 and LSD_41 diesel fuels were obtained in 2005 (before ULSD regulations of having sulfur content of no more than 15 ppm was implemented starting June 1, 2006). All diesel fuel samples were purged with nitrogen and sealed under an inert atmosphere to prevent undesired oxidation of the fuel with storage. Given the low severity of the air oxidation step, 99+% of the liquid product was recovered for both model and real fuels after the reaction. This demonstrates that undesired oxidation of fuel to gas phase products is not significant under the conditions employed in this study.

Model diesel fuel (MDF) used in this study contained equimolar concentration (3.12 μmol/g) of organosulfur compounds and naphthalenes. To mimic real diesel fuel, 10% of *tert*-butylbenzene was also added to a solvent which was a mixture of decane and hexadecane. Sulfur and aromatic compounds present in the model fuel were benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), naphthalene (Nap), and 2-methylnaphthalene (2-MNap), respectively.

LSD_41 diesel fuel containing peroxides generated by the above stated procedure was then tested for oxidation of S compounds present in it. Peroxide content in LSD_41 was adjusted for different oxidant to sulfur (O/S) molar ratios by diluting oxidized LSD_41 with unoxidized LSD_41.

The oxidation reactivity of sulfur compounds under various O/S molar ratios was first studied in a 20 mL glass batch reactor equipped with a temperature controller, a condenser, and magnetic stirrer. Typically, 5 g of air oxidized LSD-41 with varying molar ratio of peroxide generated in situ was heated at 40 °C, then 0.025 g of catalyst was added, and reaction was carried out for 15 min.

Oxidation of sulfur compounds in LSD_41-containing peroxides generated in situ was performed in a fixed bed quartz reactor. Typically, the reactor was loaded with 0.2 g of catalyst. Before the catalytic experiments, the catalysts were dried in situ at atmospheric pressure in nitrogen flow at 125 °C for 1 h, after which the temperature was decreased to the reaction temperature (40−80 °C). A high pressure liquid chromatography pump was used to measure and pump the liquid hydrocarbon feedstock. Oxidation reaction was carried out at atmospheric pressure, a weight-hourly space velocity (WHSV) of 2.4−38 h^{-1}, an oxidant/S molar ratio of 25, and a reaction temperature of 40−80 °C. Catalytic activity were recorded at specific time on stream of 4 h for fixed bed sulfur oxidation reactions, and samples were collected every 1 h. As the oxidation of sulfur compounds by peroxides generated in situ is an addition reaction as presented in Figure 1, complete product recovery was achieved. This was confirmed by weighing the products collected every hour and comparing them against feed inlet flow rate. Conversion of sulfur to oxidized sulfur after oxidation, peroxide consumption at the end of the reaction, and selectivity of peroxide for oxidation of sulfur compounds were estimated by the following formulas:

$$\mathrm{sXi} = \left[\frac{(\mathrm{sCi,\ f} - \mathrm{sCi,\ p})}{\mathrm{sCi,\ f}}\right]_{\mathrm{O/S=Z}} \times 100$$

where sXi = % of sulfur oxidized, sCi,f = sulfur concentration in the feed, sCi,p = (sulfur − oxidized sulfur) concentration in the product after reaction and was quantified by removing oxidized sulfur compounds generated after oxidation by adsorption over silica gel adsorbent (Davisil, grade 635; pore size, 60 Å; 60−100 mesh from Sigma Aldrich) followed by total sulfur analysis of the product, and Z = oxidant to sulfur molar ratio.

$$\mathrm{pXi} = \left[\frac{(\mathrm{pCi,\ f} - \mathrm{pCi,\ p})}{\mathrm{pCi,\ f}}\right]_{\mathrm{O/S=Z}} \times 100$$

where pXi = % of peroxide consumed, pCi,f = peroxide concentration in the feed, and pCi,p = peroxide concentration in the product after reaction.

$$\text{selectivity,}\ \ \mathrm{Yi} = \left[\frac{\mathrm{sXi}}{\mathrm{pXi}}\right]_{\mathrm{O/S=Z}} = \left[\frac{\%\text{ of sulfur oxidized}}{\%\text{ of peroxide consumed}}\right]_{\mathrm{O/S=Z}} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Air Oxidation of Alkyl Aromatic Compounds over CuO Catalysts. Bulk and supported CuO based catalysts were first evaluated for liquid phase oxidation of pure isopropylbenzene (IPB) to IPB hydroperoxide at 120 °C using air as an oxidant under atmospheric pressure. All catalysts were calcined at 450 °C in air before liquid phase oxidation tests and were tested on an equal weight basis. The performances of the catalysts along with their BET surface area and pore volume are shown in Table 1. A blank liquid phase oxidation of IPB without any catalyst was also carried out under the same conditions.

As shown in Table 1, $10CuO/Al_2O_3$, $CuO-ZnO/Al_2O_3$, and unsupported CuO showed considerable activity for oxidation of IPB. Under the conditions tested, about 20.3 and 16.4 wt % of IPB was oxidized over $10CuO/Al_2O_3$ and $CuO-ZnO/Al_2O_3$ catalysts, respectively. Even though these catalysts showed the highest activity among the catalysts tested, selectivity to formation of IPB hydroperoxide was only 29.0 and 43.5% over $10CuO/Al_2O_3$ and $CuO-ZnO/Al_2O_3$ catalysts, respectively. In contrast to the Al_2O_3 based supported catalysts, the hydroperoxide selectivity over unsupported CuO catalyst was 80.6%. The lower selectivity observed over Al_2O_3 supported catalysts might be due to further decomposition of IPB hydroperoxide to oxidized products such as acetophenone and 2-phenyl-2-propanol, which have been observed in previous studies during both heterogeneous and homogeneous liquid phase oxidation of IPB.[17,18] It might be plausible that the better dispersion of CuO on Al_2O_3 support results in conversion of IPB hydroperoxides to undesired products. Other oxygenates formed during liquid phase air oxidation of IPB were not identified in this study as IPB hydroperoxide was the primary product of interest. Although the selectivity for IPB hydroperoxide was the highest on the unsupported CuO catalyst, conversion was relatively lower (9.3%) when compared to Al_2O_3 supported catalyst. Nevertheless the highest hydroperoxide yield was obtained on the unsupported CuO catalyst, as shown in Table 1. It should be noted that although other oxygenates were not identified in this study, future research directed toward identification of oxygenates by the proposed process is required. This would be important in real diesel fuels to understand the effect of produced oxygenates on stability and corrosion properties. In comparison to Al_2O_3 supported and unsupported CuO catalyst, conversion of IPB over SiO_2 and TiO_2 based supports was negligent and the activity of these catalysts was comparable to that of the blank liquid phase oxidation run, or even worse (in the case of $10CuO/SiO_2$ catalyst). Liquid phase alkylaromatic oxidation is a free radical reaction, and it is probable that the nature of CuO sites on SiO_2 retard the formation of free radical required to propagate the reaction.

To understand the nature of the active phase on supported and unsupported CuO catalysts, calcined catalysts were analyzed by H_2-TPR and the profiles are shown as Figure 2. Relative to the unsupported CuO catalyst, the supported catalysts are characterized by low temperature reduction peaks indicating well dispersed CuO species. The low activity catalysts, $10CuO/SiO_2$ and $10CuO/TiO_2$, were characterized only by the presence of low temperature H_2-TPR peaks between 150 and 275 °C potentially indicating isolated cupric ions,[19] which is in contrast to supported Al_2O_3 based catalyst and unsupported CuO catalyst. In addition to the low temperature H_2-TPR peak, a high temperature TPR peak between 300 and 400 °C was observed on $10CuO/Al_2O_3$ indicating the formation of dispersed CuO and $CuAl_2O_4$ type species.[20] Bulk CuO species which are evident in the 400 °C range for the unsupported CuO catalyst was not observed on the $10CuO/Al_2O_3$ catalyst. On the $CuO-ZnO/Al_2O_3$ catalyst, the TPR peak between 300 and 400 °C was not observed but a low temperature peak centered on 280 °C was prevalent. As seen from Table 1, the highest selectivity for IPB hydroperoxide formation was obtained over unsupported CuO catalyst which was characterized by the presence of the bulk CuO phase. The highest activity for IPB oxidation or conversion was obtained over $10CuO/Al_2O_3$ catalyst which was characterized by the presence of dispersed and mixed oxide phase as discussed earlier. So tailoring a material containing bulk, dispersed, and mixed CuO phases can potentially lead to a catalyst with high activity for oxidation of IPB along with high selectivity toward IPB hydroperoxide formation.

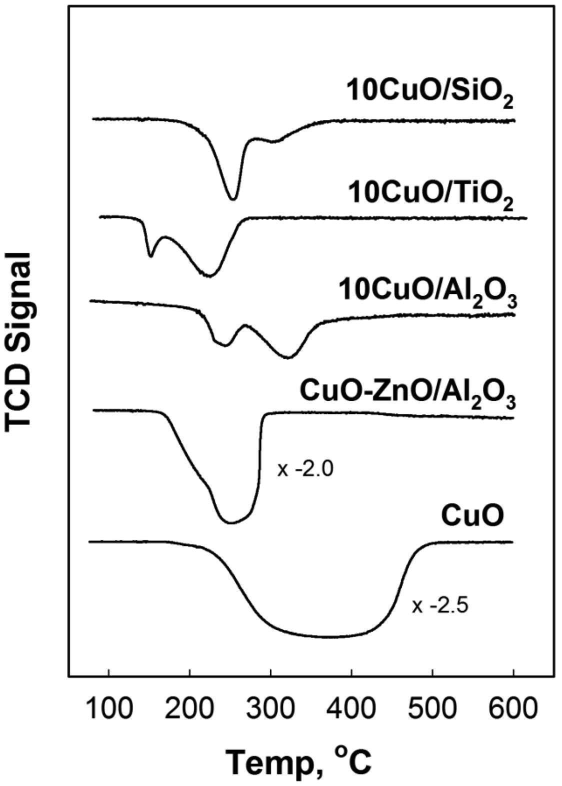

Figure 2. H_2-TPR profiles of supported and bulk CuO based catalysts.

As unsupported CuO catalyst gave the highest yield and selectivity for hydroperoxides among catalysts tested, it was further tested to study the effect of aromatic structure on activity for hydroperoxide formation. Toward this, isopropylbenzene (IPB), cyclohexylbenzene (CHB), *sec*-butylbenzene (*sec*-BB), and 2-isopropylnaphthalene (IPN) dissolved individually in decane at 30 wt % were tested for liquid phase oxidation using air.

Figure 3 shows the effect of the type of alkyl aromatic compounds on peroxide yield and peroxide stability with reaction time during liquid phase air oxidation catalyzed by unsupported CuO. As seen from Figure 3, the peroxide yield decreases in the order of IPB > CHB ≈ *sec*-BB ≫ IPN. In liquid phase air oxidation up to about 150 °C, the generalization is that tertiary C−H is attacked more easily than the secondary C−H and primary is most difficult for oxidation.[21] This is in line with the general postulation that the most stable free radical will be the one formed, and this represents the initiation step of the liquid phase air oxidation process.[16,21] From Figure 3, it is evident that tertiary-alkyl substituted IPB is far more reactive for liquid phase air oxidation than secondary-alkyl substituted CHB and *sec*-BB in the presence of decane as the solvent. Also, stability of hydroperoxides is in line with their ease of formation and under the conditions tested, and as seen from Figure 3, tertiary-alkyl substituted benzene, IPB, is the most stable among the alkyl aromatic compounds tested. Secondary-alkyl substituted benzene, CHB, showed relatively poor stability as evident from the decrease in peroxide yield

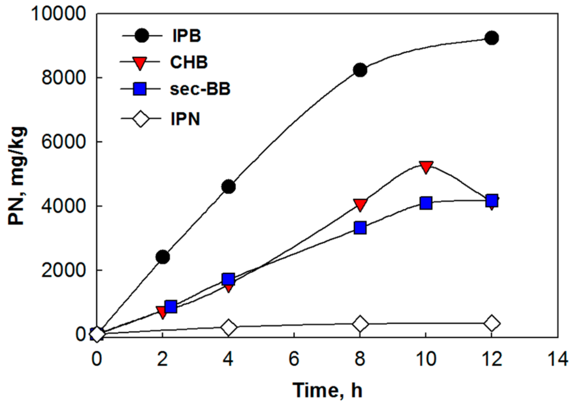

Figure 3. Effect of the type of alkyl aromatic compounds on peroxide yield in model diesel fuel (containing 30 wt % aromatic compound in decane) with reaction time (reaction conditions: 40 g of model diesel fuel; 1.6 g of catalyst; temperature, 120 °C; air flow rate, 220 mL/min).

after 10 h of reaction time. It has been observed in previous studies that two-ring and three-ring aromatics such as naphthalene and anthracene are effective inhibitors of oxidative attack through the formation of resonance stabilized radicals.[21] IPN did not exhibit significant activity for liquid phase air oxidation under the conditions where alkyl substituted benzenes were reactive. This shows that the alkyl substituted benzenes in real liquid hydrocarbon fuels are more likely to be the precursors for generating peroxides if tested under similar conditions. Also no significant oxidation of the decane employed as solvent was observed which was confirmed by GC-FID analysis.

3.2. Air Oxidation of Aromatics in Diesel Fuel over CuO Catalysts. Since unsupported CuO catalyst gave the highest activity for alkyl substituted benzenes in surrogate fuel, it was further tested for liquid phase oxidation of three different diesel fuels using air to obtain peroxides in situ. Three diesel fuels, viz., LSD_350, LSD_41, and ULSD_15, were obtained from different sources and their corresponding sulfur levels were 350, 41, and 15 ppmw, respectively. Figure 4 presents the effects of reaction time on the yield of peroxides from the three diesel fuels during liquid phase air oxidation in the presence of CuO catalyst. As seen from Figure 4, unsupported CuO was effective in liquid phase air oxidation of the three real diesel fuels but with varying activity. This variation in activity was consistent with surrogate fuel liquid phase air oxidation discussed above and shown in Figure 3 where the effect of the aromatics type on peroxide yield was discussed. The type of aromatics can have a significant effect on peroxide yield, but real diesel fuel is a mixture of different aromatics, paraffins, and cycloparaffins with individual composition and content varying with source. As diesel fuels obtained in this study were from three different sources, variation in activity for peroxide formation demonstrates the potential difference in their composition. A detailed compositional analysis of the fuel can potentially shed fundamental insight on the difference in activity for peroxide formation among diesel fuels tested in this study. But it should be noted that the presence of other two-ring and three-ring aromatics can inhibit oxidation of alkyl substituted benzene and can potentially have a profound effect on the stability of the alkyl substituted benzene hydroperoxide generated. More detailed study would be required for understanding the effects of other multiring aromatics on oxidation of alkyl substituted benzene. This shows the composition of the feedstock, especially the composition of alkylated aromatics which are the potential precursors for hydroperoxide formation in diesel fuel, might be more critical for producing oxidants in situ. To meet several other product specifications other than sulfur, diesel fuel as a final product is obtained by blending upgraded middle distillate from various units in a refinery. The composition of blending can determine the type and amount of reactive alkyl substituted benzenes in diesel fuel which can determine the activity of the stream for liquid phase air oxidation to produce hydroperoxides. As stated earlier, even though different model aromatic compounds were tested for liquid phase air oxidation to produce hydroperoxides in this study, a future study on detailed compositional analysis of the real diesel fuel is required to understand the factors affecting the generation of hydroperoxides in situ by air oxidation.

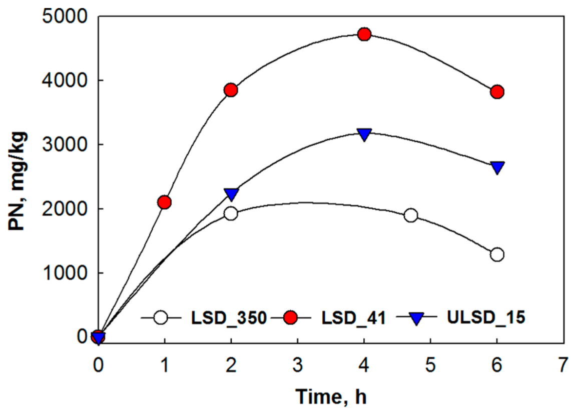

Figure 4. Yield of peroxides from air oxidation of diesel fuels obtained from different soruces (reaction conditions: 40 g of diesel fuel; 1.6 g of unsupported CuO catalyst; temperature, 120 °C; air flow rate, 220 mL/min).

3.3. Catalytic Oxidation of Sulfur in Model Fuel over MoO_3 Catalysts. Before studying the activity for peroxide generated in situ for selective oxidation of sulfur compounds in real diesel fuel, a surrogate diesel fuel containing representative organosulfur and sulfur free aromatics in equimolar concentrations was tested for oxidation to understand the selectivity of sulfur oxidation using IPB hydroperoxide as oxidant. In an effort to replicate a diesel fuel, 10 wt % of *tert*-butylbenzene was also added to the paraffinic solvent composed of decane and hexadecane. Since IPB hydroperoxide is a commercially available material, 80% IPB hydroperoxide or cumene hydroperoxide (CHP) in IPB was obtained from Sigma Aldrich and used as such for selective oxidation of sulfur compounds in the surrogate diesel fuel. Selective oxidation experiment was carried out in a batch reactor in the presence of $15MoO_3/SiO_2$ catalyst for 30 min, and no air was co-fed as an oxidant. As seen from Table 2, CHP is highly effective in selective oxidation of sulfur compounds in the surrogate diesel fuel. Oxidation of sulfur compounds by CHP shows higher reactivity for DBTs and methyl substituted DBTs than BT type sulfur compounds, which is consistent with several previous studies.[7,8]

No enhanced effect on oxidation reactivity because of methyl substituent in DBT was observed in this study which shows that steric hindrance might play a role in selective oxidation using alkyl substituted benzene hydroperoxide and heterogeneous catalyst. The observation that DBT is more reactive for

Table 2. Oxidation of Representative Sulfur and Sulfur Free Aromatic Compounds Using CHP as Oxidant[a]

compd	BT	DBT	4-MDBT	4,6-DMDBT	Nap	2-MNap
initial concn (μmol/g)	3.12	3.12	3.12	3.12	3.12	3.12
concn of S, ppmw	100	100	100	100		
oxidation, mol %	36.0	92.9	93.6	91.3		

[a] Reaction conditions: 5 g of MDF; 0.03 g of 15% MoO_3/SiO_2 catalyst; temperature, 80 °C for 30 min.

oxidation is consistent with a recent study by Stanger and Angelici where they observed that DBT is oxidized faster than 4,6-DMDBT by *tert*-butyl hydroperoxide (TBHP) catalyzed by silica.[22] Although, by theory, the electron density on the sulfur atom for 4,6-DMDBT is higher than DBT because of the methyl substituents, the methyl group in 4,6-DMDBT might sterically hinder the sulfur atom in a heterogeneous based catalytic oxidation. This can result in DBT being more reactive than 4,6-DMDBT. As presented in Table 2, the presence of one methyl substituent does not have an adverse effect on activity and 4-MDBT is more reactive than DBT for oxidation under the same conditions tested in this study. No oxidation of naphthalene and 2-methylnaphthalene were observed using CHP as oxidant in the presence of $15MoO_3/SiO_2$ catalyst.

3.4. Catalytic Oxidation of Sulfur in Model Fuel over MoO_3 Catalysts. Given the effectiveness of alkyl substituted benzene hydroperoxide for oxidation of model sulfur compounds, sulfur compounds in a real diesel fuel were tested for oxidation using peroxides generated in situ. Toward this, LSD_41 diesel fuel was air oxidized to different peroxide levels by using unsupported CuO catalyst under conditions as described in Figure 4. Oxidation of sulfur compounds was then carried out over $15MoO_3/SiO_2$ catalyst using LSD_41 with different levels of peroxides. Figure 5 shows the effect of peroxide amount generated in situ on the oxidation activity for sulfur compounds. As seen in Figure 5, to obtain 90% oxidation of sulfur compounds in LSD_41 diesel by peroxides generated in situ, the O/S molar ratio required was 28. A similar study carried out by Ishihara et al. using *tert*-butyl hydroperoxide (TBHP) as an oxidant showed that about 87% of the sulfur compounds present in a light gas oil (initial sulfur concentration of 39 ppmw) can be oxidized at 80 °C with an O/S molar ratio of 16.[8] Although it was a different study with different feed employed, it shows that the amount of peroxide required for effective oxidation of sulfur compounds varies with the type of peroxide used. Since, in this study, peroxides were generated in situ by air oxidation, the stability and activity of the peroxides for oxidation can vary as real diesel fuel can contain different types of alkyl aromatics. Also, the general trend in higher O/S molar ratio required for complete oxidation of sulfur compounds in real diesel feeds has been attributed to the consumption of oxidant by other reactive components in the real feed. Theoretical O/S molar ratio is 2 for complete oxidation of sulfur compounds, but it has been postulated that olefins, nitrogen compounds, or other polyaromatic hydrocarbons can be reactive toward peroxide oxidation as well.[8] But as seen from Table 2, two-ring aromatics are not reactive toward oxidation under conditions where sulfur oxidation is reactive. Detailed study on oxidation of other aromatic compounds such as three-ring aromatic and nitrogen-containing compounds are required to understand the increased peroxide consumption for real diesel fuels. Nevertheless 90% oxidation of sulfur compounds in real diesel fuel LSD_41 was feasible by generating peroxides in situ using air without any addition of pure organic peroxides.

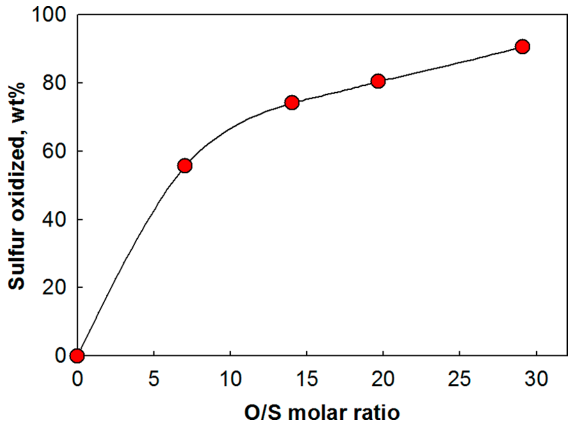

Figure 5. Effect of concentration of in situ generated peroxides on oxidation of sulfur compound in diesel fuel LSD_41 (reaction conditions: 3 g of LSD_41 containing peroxide generated in situ; 0.03 g of $15MoO_3/SiO_2$ catalyst; temperature, 40 °C for 30 min).

As liquid phase oxidation of alkyl aromatics in decane using air and unsupported CuO catalyst was carried out in the absence of sulfur compounds, the state of sulfur compounds after liquid phase air oxidation of real diesel fuel was investigated by sulfur selective GC-PFPD. The state of the sulfur compounds in diesel fuel LSD_41 during different stages of oxidation is presented as Figure 6. As shown in the first chromatograph, LSD_41 before oxidation contained predominantly alkyl substituted dibenzothiophenes, which are hard to remove sulfur compounds by conventional hydrotreating process under low severity conditions. The second chromatograph shows the state of the sulfur compounds after liquid

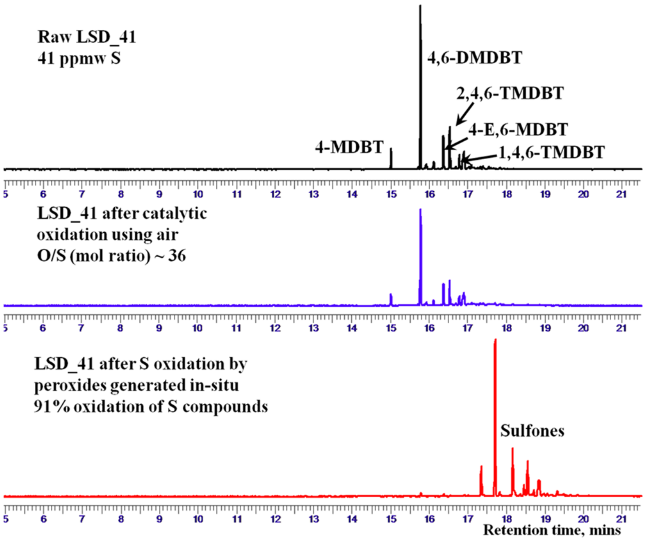

Figure 6. Oxidation of sulfur compounds in LSD_41 by two-step procedure. The PFPD chromatograph in black indicates the type of sulfur compounds in LSD_41, blue indicates there was no significant conversion of sulfur compounds during peroxide generation by air oxidation, and red indicates oxidized sulfur compounds produced by oxidation of sulfur compounds using peroxides generated in situ.

phase air oxidation of LSD_41 using unsupported CuO catalyst. As shown in the inset of the chromatograph, peroxides generated in situ corresponded to O/S molar ratio of 36. This was to ensure that enough peroxides are present to enable complete oxidation of sulfur compounds based on Figure 5. Oxidation of sulfur compounds was then carried out over $15MoO_3/SiO_2$ catalyst using peroxides generated in situ, and the third chromatograph (bottom) shows the state of the sulfur compounds after selective oxidation. As shown in Figure 6, liquid phase air oxidation of LSD_41 does not result in any significant oxidation of sulfur compounds to oxidized sulfur compounds. This can be seen by the absence of any shift in sulfur peaks after liquid phase air oxidation of LSD_41. But selective oxidation of sulfur compounds using peroxides generated in situ results in almost complete conversion of alkyl substituted dibenzothiophenes as seen from the shift in the retention time of sulfur compounds.

Since peroxides used in this study are a mixture of different alkyl substituted aromatic peroxides originating in a real liquid hydrocarbon fuel, the effect of support on the activity of molybdenum oxide for oxidation of sulfur compounds was evaluated. Two different catalysts, viz., MoO_3/SiO_2 and MoO_3/Al_2O_3 catalysts with varying loading of molybdenum oxide, were tested. MoO_3/Al_2O_3 was selected as the reference catalyst as it has been shown in previous studies to be the most active catalyst for oxidation of sulfur compounds using *tert*-butyl hydroperoxide as the oxidant.[8] The catalysts were evaluated for oxidation of sulfur compounds (using peroxides generated in situ by liquid phase air oxidation of LSD_41 diesel fuel using unsupported CuO catalyst) in LSD_41 real diesel fuel at 40 °C for 15 min in a batch reactor without any flow of air. Oxidant to sulfur molar ratio was fixed at 20 for all cases. All the catalysts were tested on an equal weight basis and were calcined at 550 °C in air before sulfur oxidation tests. The sulfur oxidation performances of the catalysts using peroxide generated in situ are presented in Figure 7.

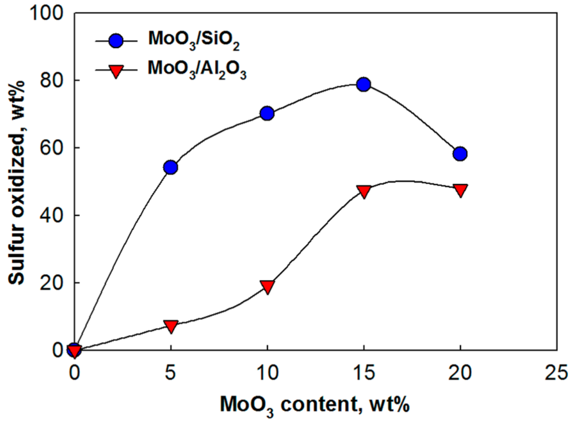

Figure 7. Effect of MoO_3 content on oxidation activity of sulfur compounds in LSD-41 over SiO_2 and Al_2O_3 supported catalyst (reaction conditions: 3 g of LSD_41 containing peroxide generated in situ; 0.03 g of catalyst; temperature, 40 °C for 15 min).

Relative to Al_2O_3 supported catalyst, SiO_2 supported catalyst showed higher activity for oxidation of sulfur compounds in LSD_41 diesel fuel under all molybdenum oxide loadings. The higher activity of SiO_2 supported catalyst was especially dominant at lower loadings of molybdenum oxide. For example as seen from Figure 7, at 5% loading of molybdenum oxide, about 58% of sulfur compounds in LSD_41 were oxidized with SiO_2 as the support whereas <10% of the sulfur compounds were oxidized over Al_2O_3 as the support. With increasing loadings, the effect of support on activity seems to disappear and both supports showed almost similar activity at molybdenum oxide loading of 20%.

To elucidate the effect of support on activity of molybdenum oxide catalyst for oxidation of sulfur compounds, the catalysts were characterized by XRD and H_2-TPR. XRD patterns of SiO_2 and Al_2O_3 supported MoO_3 catalysts under various loadings are presented in Figure 8. In contrast to SiO_2 supported catalyst where crystalline molybdenum oxide species are present at all MoO_3 loadings, crystalline molybdenum oxide species are present only in the high Al_2O_3 15% and 20% MoO_3 catalysts. This is consistent with previous observation that bulk molybdenum oxide interacts weakly with SiO_2 resulting in formation of dispersed MoO_3 even at lower loadings.[23] The absence of crystalline molybdenum oxide species in low Al_2O_3 5% and 10% MoO_3 catalysts indicate the strong interaction of molybdenum oxide with Al_2O_3 resulting in a well dispersed multilayer of molybdenum oxide. Al_2O_3 supported samples also exhibit diffraction line characteristics of γ-Al_2O_3 and $Al_2(MoO_4)_3$ although the later becomes dominant only at higher loadings of molybdenum oxide.

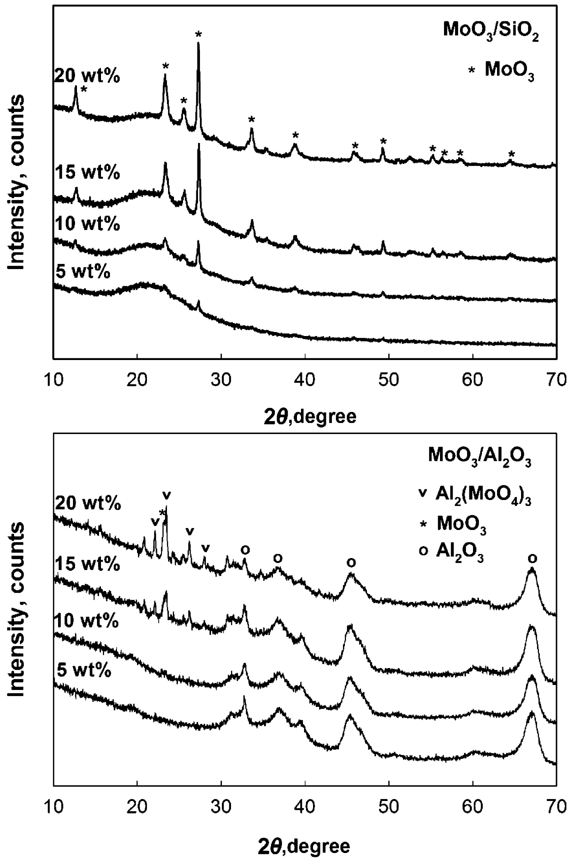

Figure 8. Powder X-ray diffraction patterns of silica and alumina supported MoO_3 catalysts at various MoO_3 loadings.

To understand the effect of support on reducibility of the catalysts, SiO_2 and Al_2O_3 supported MoO_3 catalysts under various loadings were also characterized by H_2-TPR and the spectra are presented in Figure 9. The SiO_2 supported catalyst yields a two-peak pattern, and the Al_2O_3 supported catalyst

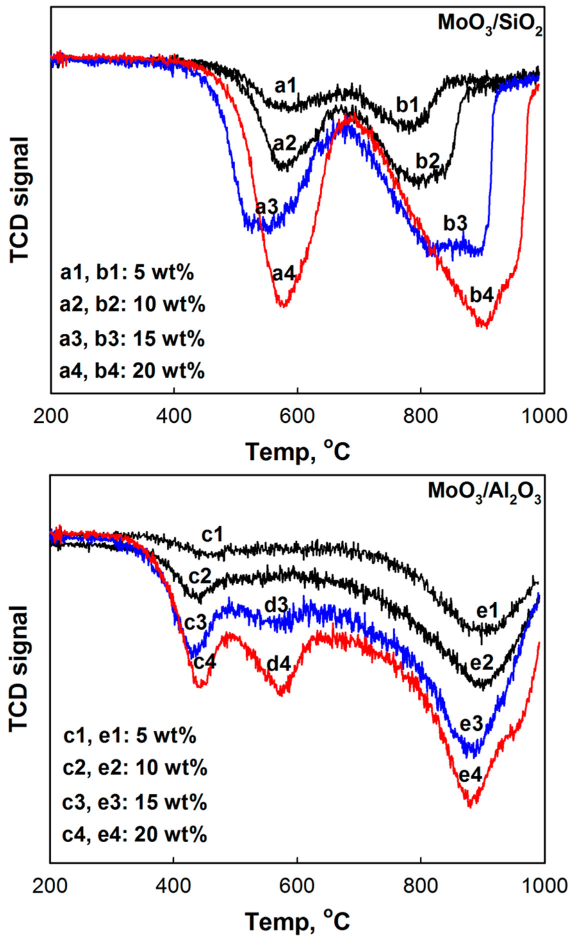

Figure 9. H_2-TPR profiles of silica and alumina supported MoO_3 catalysts at various MoO_3 loadings.

yields a three-peak pattern. SiO_2 supported catalyst is characterized by the presence of the first T_{max} peak between 520 and 600 °C (peak a) indicating weak interaction between SiO_2 and MoO_3 resulting in dispersed MoO_3. The first T_{max} peak for Al_2O_3 is observed at relatively lower temperatures between 420 and 460 °C (peak c) indicating strong interaction which is attributed to multilayer of molybdenum oxide, consistent with previous studies. This multilayer must be distinguished from the dispersed MoO_3 observed on SiO_2 as reported by Rajagopal et al. who investigated molybdenum catalysts on different supports.[23] As the molybdenum loading is increased to 15% on both supports, the first T_{max} peaks of SiO_2 (peak a) and Al_2O_3 (peak c) shift to lower temperature, and this corresponds to decreased interaction of molybdenum oxide with support with increasing loading. But at 20% MoO_3 loading, this trend reverses and the first T_{max} peak on both catalysts shifts to higher temperature which might be due to poor dispersion of molybdenum oxide at higher loadings. In the Al_2O_3 supported 15% and 20% MoO_3 catalysts, a second T_{max} peak is observed between 560 and 580 °C (peak d). This temperature window is similar to the first T_{max} peak of SiO_2 supported catalysts and represents the characteristics of dispersed MoO_3 phase at higher loadings because of decreased interaction with Al_2O_3 at higher loadings. This was also evident from XRD analysis of these catalysts where crystalline molybdenum oxide was observed as seen in Figure 8. The high temperature T_{max} peaks for SiO_2 supported (peak b) and Al_2O_3 supported (peak e) catalysts represent bulk MoO_3 and $Al_2(MoO_4)_3$ phases, respectively. The combination of XRD and H_2-TPR data along with sulfur oxidation activity data shown in Figure 7 indicates that interaction of molybdenum oxide with the support is vital for oxidation activity. This shows that molybdenum oxide based catalysts which have a weak interaction with the support such as SiO_2 might be more preferred.

As SiO_2 supported and Al_2O_3 supported catalysts with 15% MoO_3 loading gave the highest activity for oxidation of sulfur compounds under batch conditions at 40 °C, they were further evaluated to study the effect of temperature on selectivity for oxidation of sulfur compounds in a fixed bed reactor. Both catalysts were tested for activity and selectivity in oxidation of sulfur compounds in LSD_41 real diesel containing peroxides generated in situ equivalent to an O/S molar ratio of 25 by varying temperatures (40, 60, and 80 °C) at constant WHSV of 12 h^{-1}. To generate peroxides in situ, LSD_41 real diesel fuel was preoxidized in a batch reactor using unsupported CuO catalyst at 120 °C with a flow of air. For evaluation of activity of peroxides generated in situ for oxidation of sulfur compounds, no air was flowed through the fixed bed reactor. Highest activity and selectivity for oxidation of sulfur compounds was observed using $15MoO_3/SiO_2$ catalyst at 40 °C. Temperature had negligible effect on $15MoO_3/SiO_2$ catalyst activity as no increase in the rate of oxidation was observed by increasing the temperature to 60 and 80 °C, potentially due to undesired decomposition of peroxides over $15MoO_3/SiO_2$ catalyst at higher temperatures.

Table 3. Kinetic Parameters and Selectivity of SiO_2 and Al_2O_3 Supported MoO_3 Catalysts for Oxidation of Sulfur Compounds in Real Diesel Fuel[a]

catalyst	oxidant	temp, °C	$k \times 10^{-3}$,[b] g of S/((g of cat)·s)	selectivity[c], %	note
$15MoO_3/SiO_2$	peroxide generated in situ	40	2.6	81.5	current study
		60	1.8	51.1	
		80	1.9	47.2	
$15MoO_3/Al_2O_3$	peroxide generated in situ	40	0.5	42.9	
		60	1.0	54.6	
		80	1.8	51.2	
$15MoO_3/Al_2O_3$	TBHP	40	3.0	NA[d]	ref[8]
		60	6.1		
		80	17.0		

[a] Reaction conditions: LSD_41 containing peroxide generated in situ (O/S = 25 after air oxidation at 120 °C for 1 h); atm pressure; WHSV, 12 h^{-1}. [b] k = rate constant. [c] Selectivity = $[(\% \text{ of sulfone produced})/(\% \text{ of peroxide consumed})]_{O/S=25} \times 100$. [d] NA: not available.

Table 3 shows the first order rate constant for oxidation of sulfur compounds using peroxides generated in situ over 15MoO_3/SiO_2 and 15MoO_3/Al_2O_3 catalysts. Relevant kinetic data obtained from literature by oxidation of sulfur compounds using TBHP as oxidant over 15MoO_3/Al_2O_3 catalyst are also included in Table 3. The type of oxidant has a significant impact on the oxidation of sulfur compounds.

Under comparable conditions, the rate constant for oxidation of sulfur compounds was much slower using peroxides generated in situ in comparison with TBHP[8] as oxidant over 15MoO_3/Al_2O_3 catalyst [0.5×10^{-3} g of S/((g of cat)·s) versus 3.0×10^{-3} g of S/((g of cat)·s), respectively, at 40 °C]. At 40 °C, 15MoO_3/SiO_2 was almost 5 times more active than 15MoO_3/Al_2O_3 for oxidation of sulfur compounds using peroxides generated in situ as observed from the rate constant data [2.6×10^{-3} g of S/((g of cat)·s)]. Increasing activity for sulfur oxidation by TBHP over 15MoO_3/Al_2O_3 catalyst with temperature is evident from the rate constant data [17.0×10^{-3} g of S/((g of cat)·s) at 80 °C] presented in Table 3. In contrast to TBHP as oxidant, relatively poor rates were observed for oxidation of sulfur compounds at 80 °C while using peroxides generated in situ as oxidants on both 15MoO_3/Al_2O_3 and 15MoO_3/SiO_2 catalysts. This difference in trend between peroxides generated in situ and TBHP reflects the difference in the nature of their stability and selectivity for oxidation of S compounds. The activation energy with 15MoO_3/Al_2O_3 as catalyst was measured as 24.3 kJ/mol. Since the activity of 15MoO_3/SiO_2 catalyst for oxidation of sulfur compounds by peroxides generated in situ decreased with an increase in temperature, temperature conditions employed in this study were not suitable for measuring the activation energy over 15MoO_3/SiO_2 catalyst. As discussed below, with an increase in temperature 15MoO_3/SiO_2 catalyst is less selective for oxidation of sulfur compounds and is more active toward undesired decomposition of peroxides. This shift in selectivity with temperature results in a negative effect on the rate of the oxidation reaction over 15MoO_3/SiO_2 catalyst.

Selectivity of peroxides generated in situ for oxidation of sulfur compounds presented in Table 3 was estimated by measuring the peroxide content of the LSD_41 diesel fuel before and after sulfur oxidation over 15MoO_3/SiO_2 and 15MoO_3/Al_2O_3 catalysts in the fixed bed reactor. The highest selectivity for oxidation of sulfur compounds was observed over 15MoO_3/SiO_2 catalyst at 40 °C. Even at 40 °C, ~18.5% of peroxides are decomposed to other oxygenates as presented by selectivity data in Table 3. Increasing reaction temperature to 60 and 80 °C had a detrimental effect on the selectivity of 15MoO_3/SiO_2 catalyst. Relatively poor selectivity was observed over 15MoO_3/Al_2O_3 catalyst at all reaction temperatures. Poor selectivity over 15MoO_3/Al_2O_3 catalyst and at higher temperatures over 15MoO_3/SiO_2 catalyst reveal that, even at O/S molar ratio of 25, undesired decomposition of peroxides takes place under those conditions.

It should be noted that, under blank conditions, minimal decomposition of peroxides and no activity for sulfur oxidation was observed for the preoxidized LSD_41 diesel fuel. This indicates that MoO_3 based catalyst also causes undesired decomposition of peroxides to potentially other oxygenates under the conditions employed in this study. The selectivity of MoO_3 catalyst to cause undesired decomposition of peroxides can be inferred from the selectivity data presented in Table 3.

Plots of $\ln(C_A/C_0)$ versus 1/WHSV for oxidation of sulfur compounds by peroxides generated in situ at 40 °C over 15MoO_3/SiO_2 and 15MoO_3/Al_2O_3 catalysts were obtained and are presented in Figure 10. C_A/C_0 is defined as the ratio of total sulfur concentration of unoxidized or unconverted sulfur compounds to the initial sulfur concentration. A linear relationship was obtained under the reaction conditions tested, as shown in Figure 10, suggesting that this reaction can be treated as a first order reaction which is consistent with an earlier study on oxidation of sulfur compounds by TBHP over 15MoO_3/Al_2O_3 catalyst.[8,24]

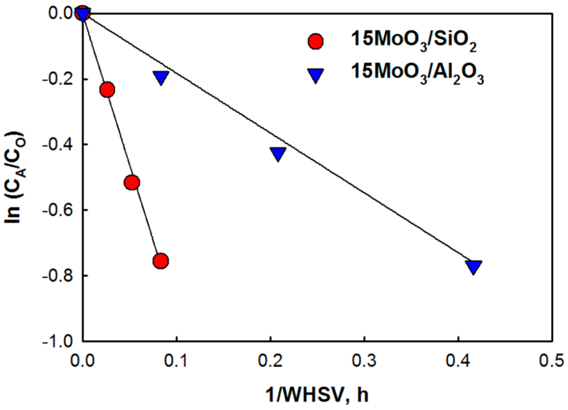

Figure 10. First order plots of $\ln(C_A/C_0)$ and reaction time for the sulfur compounds over 15MoO_3/SiO_2 and 15MoO_3/Al_2O_3 catalysts (reaction conditions: LSD_41 containing peroxide generated in situ (O/S = 25 after air oxidation at 120 °C for 1 h); atm pressure; temperature, 40 °C).

4. CONCLUSION

This study presents a novel approach to deep desulfurization of diesel fuels in two steps where air is used as oxidant for the in situ catalytic generation of hydroperoxides from aromatics in diesel fuel in the first step and the sulfur compounds are oxidized catalytically by the in situ generated hydroperoxides in the second step. The proposed two-step approach is more environmentally friendly and efficient, which does not rely on the use and storage of chemical agents such as peroxides for oxidation that are involved in most previous studies for oxidative desulfurization.

Among the bulk and supported CuO based catalysts tested for liquid phase air oxidation of surrogate and real liquid hydrocarbon fuels at 120 °C, bulk CuO gave the highest yield and selectivity for hydroperoxide of 9.5 wt % and 80.6%, respectively, by liquid phase air oxidation of isopropylbenzene at 120 °C. Analyses of catalysts by H_2-TPR revealed that although supported catalysts yield a dispersed CuO phase, the presence of bulk CuO phase might be more preferable to obtain hydroperoxide with high yield and selectivity by liquid phase air oxidation. Liquid phase air oxidation of different alkyl aromatics in decane revealed that tertiary alkyl aromatics were more active for generation of hydroperoxides than secondary alkyl aromatics. In contrast to isopropylbenzene (and *sec*-butylbenzene and cyclohexylbenzene), very low yield of hydroperoxide was obtained by liquid phase air oxidation of isopropylnaphthalene.

A different level of activity for generation of hydroperoxide was observed during liquid phase air oxidation of three diesel fuels at 120 °C in the presence of bulk CuO catalyst. Measurement of oxidation activity revealed increasing hydroperoxide yield with time followed by a decrease in hydroperoxide yield. This yield pattern was consistent with hydroperoxide yields obtained by liquid phase air oxidation of alkyl aromatic hydrocarbons dissolved in decane.

MoO_3/SiO_2 and MoO_3/Al_2O_3 catalysts are active for oxidation of sulfur compounds using hydroperoxides as oxidants generated in situ in real diesel . The support has a significant effect on activity for oxidation of sulfur compounds when molybdenum oxide loading is <15 wt %. At low molybdenum loadings, MoO_3/SiO_2 showed higher activity than MoO_3/Al_2O_3, although similar activities were obtained on both supports at MoO_3 loading of 20 wt %.

High activity and selectivity for oxidation of sulfur compounds using hydroperoxides generated in situ in real diesel fuel was obtained at 40 °C over $15MoO_3/SiO_2$ catalyst under fixed bed flow conditions. Selectivity defined as (% sulfone produced)/(% of peroxide consumed) was measured at varying reaction temperatures on both $15MoO_3/SiO_2$ and $15MoO_3/Al_2O_3$ catalysts. Relatively low selectivity was observed on both catalysts when oxidation of sulfur compounds was carried out at 60 and 80 °C using hydroperoxides generated in situ as oxidant demonstrating that low temperature oxidation of sulfur compounds is preferred while using hydroperoxides generated in situ as oxidant.

This study demonstrates that alkyl aromatic hydrocarbons in real hydrocarbon fuels can be used as the source for generating hydroperoxides in situ using air, and the hydroperoxides generated are effective as oxidants for oxidation of hard-to-remove sulfur compounds such as 4,6-dimethyldibenzothiophene into more polar moieties. The results from this study with three real diesel fuels and model compounds demonstrate that the two-step approach is feasible and effective for deep oxidative desulfurization of diesel fuels.

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Notes

The authors declare no competing financial interest.

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