Impact of Sulfation and Desulfation on NO_x Reduction Using Cu-Chabazite SCR Catalysts

D. William Brookshear^{1*}, Jeong-gil Nam², Ke Nguyen³, Todd J. Toops¹, Andrew Binder³

¹Oak Ridge National Laboratory, Oak Ridge, TN 37831 United States

²Mokpo National Maritime University, Mokpo, Republic of Korea

³University of Tennessee, Knoxville, TN 37996 United States

***Corresponding Author: Daniel W. Brookshear**

brooksheardw@ornl.gov

1-865-946-1242

2360 Cherahala Blvd, Knoxville, TN 37932

Abstract

This bench reactor study investigates the impact of gaseous sulfur on the NO_x reduction activity of Cu-chabazite SCR (Cu-CHA) catalysts at SO₂ concentrations representative of marine diesel engine exhaust. After two hours of 500 ppm SO₂ exposure at 250 and 400°C in the simulated diesel exhaust gases, the NO_x reduction activity of the sulfated Cu-CHA SCR catalysts is severely degraded at evaluation temperatures below 250°C; however, above 250°C the impact of sulfur exposure is minimal. EPMA shows that sulfur is located throughout the washcoat and along the entire length of the sulfated samples. Interestingly, BET measurements reveal that the sulfated samples have a 20% decrease in surface area. Furthermore, the sulfated samples show a decrease in NO_x/nitrate absorption during NO exposure in a DRIFTS reactor which suggests that Cu sites in the catalyst are blocked by the presence of sulfur. SO₂ exposure also results in an increase in NH₃ storage capacity, possibly due to the formation of ammonium sulfate species in the sulfated samples. In all cases, lean thermal treatments as low as 500°C reverse the effects of sulfur exposure and restore the NO_x reduction activity of the Cu-CHA catalyst to that of the fresh condition.

Keywords: marine diesel; Cu-chabazite; NH₃ SCR; sulfur; sulfation

1. Introduction

Cu-zeolite catalysts are the leading choice for the selective catalytic reduction (SCR) of NO_x in automotive diesel engines due to their hydrothermal durability and high NO_x reduction activity over a broad temperature range. Recently, the small-pore zeolite Cu-chabazite (Cu-CHA) has been investigated and shows significant promise as the new zeolite of choice. Cu-CHA exhibits high NH₃-SCR activity and N₂ selectivity in the temperature range from 150-600°C, and shows excellent resistance to hydrothermal aging at temperatures up to 850°C [1, 2, 3, 4]. However, the possible use of Cu-CHA for NO_x abatement for maritime applications faces unique challenges. Relative to the ultra-low sulfur fuel (ULSD) used in automotive applications, which contains less than 15 ppm sulfur, marine diesel fuels have extremely high levels of sulfur, as shown in Table 1 [5]. The impact of this high sulfur content on the performance of emissions control technology must be understood in the face of increasingly stringent NO_x regulations included in the incoming MARPOL Tier II NO_x emissions standards as shown in Table 2.

Prior research has illustrated the sensitivity of Cu-zeolite SCR catalysts to the presence of sulfur in diesel exhaust [6, 7, 8, 9, 10], and it has been shown that desulfation can effectively be carried out on sulfated catalysts at temperatures above 600°C under lean exhaust conditions [11, 12]. More recently, sulfur exposure has been studied on small-pore zeolites utilizing SO_x concentrations of up to 200 ppm in simulated diesel exhaust, and it was found that SO_x can have a significant impact on the NO_x reduction activity of small-pore Cu-zeolite catalysts at evaluation temperatures below 300°C [12, 13, 14]. The primary degradation mechanisms attributed to the presence of sulfur are the formation of ammonium sulfate at temperatures less than 300°C and the adsorption of SO_x on key sites active for SCR along with the formation of copper sulfate species. Furthermore, it has been determined that SO₃ leads to more severe deactivation of the catalyst, although this is less important to maritime applications where SO₂ is

the primary component of SO_x and oxidation catalysts may not be necessary. In all cases, it was found that desulfation treatments under lean conditions at temperatures above 550°C are adequate to restore SCR activity of the sulfated catalysts.

These previous studies used SO_x concentrations between 33 and 200 ppm during sulfation of the catalysts, and achieved different levels of catalyst sulfur saturation. However, in large Category 3 marine diesel engines, which typically operate with low engine speeds and exhaust gas temperatures as shown in Table 3, the concentration of SO₂ in engine exhaust can range between 500-1000 ppm for high sulfur content fuel [15, 16]. Furthermore, while NO_x and SO_x emissions are regulated globally, CO and HC emissions from Category 3 engines are not regulated except for in the jurisdiction of the Environmental Protection Agency in waters around North America. This means diesel oxidation catalysts are not necessary for ships operating globally outside of North American waters, and thus SO₃ formation is not a primary concern for most large marine vessels containing Category 3 engines [17]. Therefore, the objective in the current study is to determine the impact of SO₂ exposure on a Cu-CHA SCR catalyst at levels which are representative of those which occur in marine diesel engines and to determine which catalytic functionality is affected. The time necessary to achieve saturation at such high levels of SO₂ is determined, and the effects of this level of sulfur are investigated through performance evaluations which measure NO_x conversion during both standard and fast SCR conditions, along with how the presence of sulfur affects other important SCR reactions such as NO to NO₂ oxidation, NH₃ oxidation, and NH₃ storage. Additionally, multiple materials characterization techniques are utilized to measure the content of sulfur in the catalyst washcoat and its impact on surface area, and DRIFTS studies are employed to identify how sulfur affects the adsorption of NO and NH₃ on the catalyst. Ultimately, this research intends to improve the understanding of sulfur exposure on Cu-zeolite based SCR catalysts, and to assess the feasibility of Cu-CHA SCR for NO_x abatement in marine diesel engines.

2. Materials and Methods

The Cu-CHA SCR catalyst in the current study has a Cu-SSZ-13 structure and is identical to that used in the exhaust system of a 2011 model year Ford-F250. Prior to sulfation, fresh SCR cores of 2.54 cm diameter and 7.62 cm length are de-greened on a bench flow reactor (BFR) in a flow consisting of 14% O₂, 5% CO₂, 5% H₂O, and N₂ balance for four hours. To simulate the high concentration of sulfur in marine diesel fuel and the conditions of the exhaust gas from marine diesel engines, sulfation is carried out at 250 and 400°C and a GHSV of 30,000 h⁻¹ with a simulated exhaust composition consisting of 500 ppm SO₂, 14% O₂, 5% CO₂, 5% H₂O, and N₂ balance for two hours, at which point the catalysts are determined to be saturated with sulfur based on measurements of SO₂ at the catalyst exit using a Midac M200 FTIR. Desulfation of SO₂-exposed catalysts is performed at different temperatures and time intervals with a lean flow composition of 14% O₂, 5% CO₂, 5% H₂O, and N₂ balance at a GHSV of 30,000 h⁻¹.

SCR performance evaluations of the sulfated and desulfated catalysts are performed on a BFR using NO_x chemiluminescence analyzers and an MKS FTIR for gas analysis. Standard and fast SCR NO_x conversion are measured at a GHSV of 30,000 h⁻¹ with a flow consisting of 14% O₂, 5% CO₂, 5% H₂O, 350 ppm NO_x, 350 ppm NH₃, and N₂ balance at temperatures from 150-300°C. The maximum evaluation temperature

of 300°C is chosen in order to avoid desulfating the catalyst during performance evaluations. NH₃ storage/oxidation and NO oxidation are measured under the same conditions by removing NO_x or NH₃ from the simulated exhaust flow, respectively.

To elucidate the deactivation mechanisms, materials characterizations are performed on the de-greened and sulfated catalysts. Electron microprobe analysis (EPMA) using a Cameca Model SC-52 is carried out on the inlet and rear of the sulfated catalysts to determine the relative concentration and distribution of sulfur in Cu-CHA washcoat. Samples of approximately 2.0 cm in length are removed from the inlet and rear of the catalysts and placed inside 2.54 cm diameter phenolic rings. Epoxy is poured over the samples and a vacuum pump is used to remove as much air as possible from the sample before the epoxy is allowed to harden overnight. To provide a flat surface for analysis, the front 1 mm of each sample is removed and the surface is polished using diamond polish to a 1 µm finish. In addition, BET surface area and pore volume measurements are obtained for de-greened, sulfated, and desulfated catalysts on a Micromeritics TriStar surface area analyzer using N₂ absorption in order to determine the impact of sulfur exposure on catalyst surface area, and inductively coupled plasma/optical emission spectrometry (ICP-OES) is used to accurately measure the total sulfur content in each of the catalyst samples (washcoat and cordierite substrate)

Diffuse-reflective infrared Fourier transform spectroscopy (DRIFTS) is utilized to study the effects of sulfur exposure on NH₃ and NO/nitrate adsorption onto the Cu-CHA washcoat surface. A small piece of catalyst is trimmed from a core and gently sanded in order to ensure the analysis surface is as flat as possible. Samples are loaded into a Harrick Praying Mantis DRIFTS reaction chamber and heated using a cartridge heater. The reaction chamber is covered by a zinc selenide (ZnSe) dome through which the infrared light from the Digilab 7000 series FTIR passes. A type-K thermocouple placed directly on the sample surface measures temperature, while a manifold of MKS mass flow controllers provides the gas mixture consisting of 10% O₂, 350 ppm of either NO or NH₃, and Ar balance.

3. Results and Discussion

3.1 Bench Flow Reactor Performance Evaluations

In order to determine an appropriate experimental protocol, three fresh Cu-chabazite SCR samples were de-greened and exposed to sulfur for 2 hours at 250°C and desulfated under lean conditions with different time and temperature combinations. This aging temperature is representative of a typical exhaust gas temperature occurring in marine diesel engines, as illustrated in Table 3.. It was decided that these samples would be evaluated for standard SCR performance using NO_x chemiluminescence analyzers to avoid sulfur exposure of the MKS FTIR used for detailed performance investigations in the remainder of the study. The results of these initial standard SCR evaluations are shown in Figure 1. Sulfur exposure at 250°C has a significant negative impact on NO_x reduction activity over the Cu-chabazite SCR catalyst, with NO_x conversion decreasing by as much as 45% between 150 and 300°C. A mild improvement in performance is seen with desulfation temperatures as low as 350°C, and after 30 minutes of desulfation at 500°C the NO_x reduction activity of the catalyst is fully restored. Based on these results, two different aging temperatures were chosen for detailed investigation using the MKS

FTIR, and it was decided that evaluation temperatures should not exceed 300°C to prevent desulfation during performance evaluation experiments. A sample sulfated for 2 hours at 250°C represents typical marine operating conditions, while a sample aged at 400°C provides insight into the impact of sulfation at higher operating temperatures where some desulfation is possible in the oxygen rich environment even while SO₂ is still present in the simulated exhaust. Additionally, two desulfated samples are fully investigated: a sample sulfated at 250°C for two hours followed by a 10 minutes desulfation at 500°C and another sulfated for two hours at 400°C and desulfated for 30 minutes at 600°C. The catalyst desulfated for 10 minutes at 500°C helps to determine a minimum threshold for the time and temperature required to restore SCR deNO_x activity to a level necessary for meeting MARPOL Tier II NO_x standards. Meanwhile, the sample desulfated at 600°C for 30 minutes is examined in order to find if it is possible to fully reverse the effects of SO₂ exposure on a Cu-CHA SCR catalyst.

Standard SCR performance for these catalysts is shown in Figure 2. SO₂ exposure has a drastic impact on the standard SCR of NO_x at temperatures below 250°C, with conversion decreasing by as much as 45% at 200°C. This is significant at the lowest operating temperatures observed in marine diesel engines where exhaust temperatures can dip as low as 200°C. Both aged samples exhibit less than 60% NO_x conversion at this temperature, which is well below the conversion required to meet the MARPOL Tier II standards. Furthermore, the lower sulfur exposure temperature results in the most significant deactivation, which agrees with results obtained by Cheng et al. who found that NO_x conversion decreases as the sulfur aging temperature is decreased, even for low levels of SO₂ exposure [12]. Mild desulfation for only 10 minutes at 500°C is not adequate to recover standard SCR performance, but after 30 minutes of desulfation at 600°C the NO_x conversion is comparable to a de-greened catalyst.

The fast SCR reaction over Cu-chabazite behaves in a unique manner relative to other Cu-zeolite SCR catalysts, and this is evident in the fast SCR performance results shown in Figure 3. At 150°C the performance of all SCR catalysts, including the de-greened sample, is below that observed under standard SCR conditions. Xie et al. attribute this phenomenon to the large kinetic diameter of NO₂, which they suggest cannot quickly enter the Cu-CHA pores to form nitrate intermediates on Cu sites and therefore blocks active sites by forming ammonium nitrate (NH₄NO₃) on Brønsted acid sites [18]. However, as the catalyst approaches the decomposition temperature of ammonium nitrate (210°C) the conversion improves. This is reflected in the performance curves in Figure 3, where NO_x conversion increases relative to standard SCR conditions for all SCR samples at evaluation temperatures of 200°C and above. In fact, once the catalyst reaches 250°C, even the most severely sulfated samples perform as well as the de-greened sample. These results agree with those obtained in studies by Kumar et al. and Wijayanti et al., who found that Cu-SAPO SCR catalysts exposed to SO_x were less impacted under fast SCR conditions relative to standard SCR conditions at evaluation temperatures above 200°C [14, 19]. The presence of NO₂ appears to lower the dependence of NO_x reduction activity on the availability of active sites since turnover on each site is sufficiently fast. This effectively lessens the sensitivity of SCR catalyst performance to the presence of sulfur when the fast SCR reaction is occurring. Additionally, this means that less desulfation time is required to recover NO_x reduction activity with NO₂ in the simulated exhaust feed, as 10 minutes of desulfation at 500°C is adequate to restore the fast SCR performance of the catalyst sulfated at 250°C. The ability to desulfate Cu-chabazite at temperatures below 600°C, with some

desulfation effects observable even at 350°C, is important to the overall performance of the catalyst system. While the catalyst is hydrothermally stable at temperatures up to 850°C, it would require a tremendous amount of fuel to achieve high desulfation temperatures for large marine diesel engines typically operating in the 200-300°C temperature window. Avoiding such a severe fuel penalty for desulfation is necessary for Cu-CHA to be a cost effective solution for NO_x abatement in these marine applications. Of course, it is likely NO₂ will only be present in significant quantities if an oxidation catalyst is used, and as mentioned earlier this may introduce its own problems with respect to SO₃ formation. It is, however, interesting to see this lack of influence of sulfur in this reaction.

In order to probe the other important reactions occurring during NH₃ SCR, evaluations for NO to NO₂ oxidation, NH₃ oxidation, and NH₃ storage are also performed. NO to NO₂ oxidation (not shown) is negligible across the evaluation temperature range used in this study, although the de-greened sample and the catalyst desulfated for 30 minutes at 600°C do display a small amount of NO oxidation at 300°C (less than 1.5%). It has previously been shown that NO to NO₂ oxidation over Cu-zeolite is minimal even at temperatures up to 600°C [20], but a recent study by Ruggeri et al. explores the mechanism of NO oxidation over Cu-CHA [21]. Utilizing in-situ DRIFTS measurements of Cu-CHA during NO+O₂ exposure, they observed the formation of nitrate and nitrite-like species which they suggest are the primary products of NO oxidative activation occurring on Cu sites over Cu-CHA. Therefore, in the current study, the small amount of NO oxidation observed during the bench flow evaluations at 300°C is believed to follow this model, and the lack of oxidation observed on sulfated catalysts is attributed to sulfur blocking the Cu sites in the catalyst washcoat.

Meanwhile, the impact of sulfur exposure on the activity for NH₃ oxidation shown in Figure 4 is significant. This effect is clearly observed at temperatures above 250°C. The de-greened sample displays the highest oxidation, with a maximum of 40% at 300°C. The activity of the sample sulfated at 400°C and desulfated for thirty minutes at 600°C is lower, but is still significant with a maximum of 22% at 300°C. Additionally, both of these samples show at least 5% NH₃ oxidation at 250°C. Meanwhile, both sulfated samples and the sample desulfated for only 10 minutes at 500°C (sulfated at 250°C) show limited NH₃ oxidation, with all three displaying less than 5% conversion at 300°C and essentially zero activity at 250°C. These results agree with Kumar et al., who also observed a decrease in NH₃ oxidation over a Cu-SAPO SCR catalyst after exposure to sulfur [14]. It is generally agreed upon that, as with NO oxidation, NH₃ oxidation in Cu-zeolite SCR catalysts occurs over active Cu sites in the washcoat [22, 23]. Thus, based upon the decreased oxidation activity for both NO and NH₃ observed over sulfated catalysts in the current study, it appears that sulfur is poisoning or blocking Cu sites in the chabazite washcoat. This is important to the SCR activity of the catalyst, as it is believed that active Cu sites play a key role during NH₃ SCR [24].

Figure 5 shows the effects of SO₂ exposure on NH₃ storage capacity of Cu-CHA SCR catalysts at temperatures of 150, 200, 250 and 300°C. The catalyst exhibiting the most reduction in the SCR performance, the sample sulfated at 250°C, displays the largest amount of NH₃ storage at all four evaluation temperatures. This is followed by the sample sulfated at 400°C and then the sample sulfated at 400°C and desulfated at 500°C for 10 minutes. The de-greened sample and the sample sulfated at 400°C and desulfated at 600°C for a full 30 minutes stored the least NH₃ across the temperature range.

While the difference amount of NH_3 storage between the de-greened, the sulfated and the heavily desulfated samples is relatively small, it appears that the amount of measured NH_3 storage is increased after sulfur exposure. This trend has been observed previously by Kumar et al. after exposure of a SAPO material based Cu-CHA SCR catalyst to 33 ppm of SO_2 for 8 hours at 200°C [14]. At temperatures below 300°C Zhang et al. attributed deactivation Cu-SAPO-34 to the formation of ammonium sulfate, which they removed at regeneration temperatures above 500°C [13]. The measured increase in NH_3 storage after sulfur exposure in the current study suggests that a similar phenomenon is occurring, with some NH_3 storing as ammonium sulfate. Further, ammonium sulfate begins to decompose at temperatures around 280°C , which is where the standard SCR performance of the Cu-CHA SCR catalysts aged in the current study improves to resemble that of the fresh sample. Therefore, the formation of ammonium sulfate at evaluation temperatures less than 250°C , followed by decomposition of ammonium sulfate at 280°C , would explain why the NO_x conversion performance of de-greened, desulfated, and sulfated catalysts are similar at 300°C .

3.2 Materials Characterization

EPMA analysis provides a way to examine the relative sulfur content and distribution in the washcoat of the catalysts exposed to SO_2 . Sulfur micrographs of fresh and sulfated samples are shown in Figures 6-8. Sulfur is not observed in the washcoat of the de-greened sample, but appears throughout the sulfated samples in similar concentrations at both the inlet and exit of the catalysts. This is confirmed by the line scans taken through the washcoat of the sulfated samples shown in Figure 9, as there is no measurable change in the average sulfur concentration from cordierite substrate to washcoat surface. While EPMA does not provide the most accurate quantitative results for the entire sample, the trends suggest that the catalyst is saturated with sulfur in both cases.

ICP-OES measurements were taken to determine the weight percentage of sulfur in the de-greened, sulfated, and desulfated catalysts (includes both washcoat and cordierite substrate). These results are shown in Figure 10. Both sulfated samples, along with the sample desulfated for 10 minutes at 500°C , contain more than 0.2 wt% sulfur, while the de-greened sample and the sample desulfated for 30 minutes at 600°C contain less than 0.05 wt% sulfur. The sample aged at 400°C shows the highest measurement of sulfur, which is somewhat surprising since it was capable of higher NO_x conversion than the sample aged at 250°C . However, if the catalysts are saturated with sulfur it would explain the similar measurements for sulfur in the sulfated samples as the two values are within 10%, which can be attributed experimental error.. Kumar et al. performed storage experiments and ICP analysis on their sulfated Cu-SAPO SCR catalysts to determine the time required to reach sulfur saturation at their feed concentration of 33 ppm SO_x and found that 12 h of sulfation achieves close to full saturation of the catalyst with a total sulfur content of between 1.5-1.8 g/ L_{cat} , with an additional 12 h of SO_x exposure making only a small difference in total sulfur uptake [14]. In the current study, the sulfated Cu-SSZ-13 samples contain between 1.2-1.4 g/ L_{cat} of sulfur, which is a similar level to that seen by Kumar et al. Based on the consistent sulfur levels observed with EPMA throughout the sulfated Cu-CHA SCR catalysts in the current study, along with the overall sulfur content measurements from ICP-OES, it is apparent that increasing the SO_2 feed in the simulated exhaust gas to match those experienced in marine diesel engines causes the SCR catalysts to become saturated with sulfur at an accelerated rate.

To determine if the sulfur present in the washcoat affected the catalytic surface, BET measurements of surface area and pore volume were taken for the de-greened, sulfated, and desulfated catalysts. The results of these measurements are shown in Figures 11 and 12, respectively. The de-greened sample has a surface area of 175 m²/g, which decreases by 20% to a value of 140 m²/g after SO₂ exposure at 250 or 400°C for two hours. Similarly, the pore volume decreases by close to 18% as a result of sulfation. The lower surface areas and pore volumes could be due to sulfur blocking access to the zeolite pores, thereby lowering N₂ adsorption during the BET measurements. After ten minutes of desulfation at 500°C the surface area and pore volume remain comparable to that of the fully sulfated catalysts. However, after thirty minutes of desulfation at 600°C both surface area and pore volume return to within 3% of the values measured for the de-greened sample. Therefore, the loss of surface area and pore volume is not due to a permanent aging or poisoning mechanism, and is recoverable if the sulfur is adequately removed from the catalyst.

3.3 DRIFTS Characterization of NH₃ and NO Adsorption

In an effort to identify what was occurring on the surface of the de-greened, sulfated, and desulfated samples, DRIFTS is used to investigate the effects of sulfur exposure on the adsorption of NO and NH₃ on the Cu-CHA catalysts. NH₃ adsorption during NH₃ + O₂ exposure generates a broad spectrum from 1200 to 4000 cm⁻¹ with multiple peaks and valleys associated with NH₃, NH₄⁺, and OH compounds on the catalyst surface [13, 24, 25, 26, 27, 28, 29, 30, 31]. While the peaks are easily identifiable in the spectra obtained in the current study (not shown), it is difficult to differentiate peak sizes among the different sulfated and desulfated samples in order to point to a clear impact of the presence of sulfur. Additionally, there are no distinct peaks which can be associated with the formation of sulfate species, such as ammonium sulfate, which seemed likely based on the increased NH₃ storage measured during performance evaluations.

While it was not possible to draw certain conclusions based on the NH₃ adsorption spectra, the absorption spectra generated during NO + O₂ exposure produce a series of distinct peaks centered around 1600 cm⁻¹ along with a small peak in the range from 2300-2100 cm⁻¹, as shown in Figures 13 and 14, respectively. From the literature, the peaks centered at 1600 cm⁻¹ can be identified as various nitrates along with NO and NO₂ adsorption on the catalyst surface [24, 25, 27, 32, 33, 34, 35], and are almost identical to those observed by Ruggeri et al. in their study on the NO oxidative properties of Cu sites in Cu-CHA SCR catalysts [21]. The intensity of these nitrate peaks is significantly higher in the de-greened sample, followed by the sample desulfated at 600°C for 30 minutes. The sample desulfated for only 10 minutes at 500°C still exhibits the primary peak at 1625 cm⁻¹, but the secondary peaks have been reduced in intensity. In the case of both sulfated catalysts, a broad low intensity peak is visible, but it is much more difficult to distinguish multiple NO_x/nitrate adsorption peaks, particularly in the sample exposed to SO₂ at 250°C. Meanwhile, the broad peaks appearing in the 2300-2100 cm⁻¹ range shown in Figure 14 are less defined, but the trends observed in peak intensity still match those occurring around 1600 cm⁻¹. This region is associated with both the formation of NO⁺ species via interaction with Cu²⁺ at 2140 cm⁻¹ and NO⁺NO₂ adducts at 2190 cm⁻¹ [21, 36]. The loss in peak intensity at both locations after sulfur exposure again suggests that the Cu sites are somehow poisoned or blocked off as a result of the presence of sulfur on the catalyst surface and in the washcoat. This same trend was observed during co-

adsorption of SO₂ and NO on Cu-SAPO-34 by Zhang et al. [13]. They concluded that the primary low temperature performance loss of Cu-SAPO-34 was ammonium nitrate formation, but also suggested that competitive adsorption of SO₂ and NO along with the formation of CuSO₄ contributed to the deactivation of the catalyst. Since SO₂ is not included in DRIFTS for the current study, it seems likely that the decrease in NO adsorption is due to blocking of the Cu sites by CuSO₄ formation or sulfate species formed during the sulfur exposure protocol. This phenomenon in conjunction with low temperature formation of ammonium sulfate during SCR evaluations would explain the poor performance of the Cu-CHA SCR catalysts sulfated in the current study.

4. Conclusions

This study examined the ability of Cu-CHA SCR to meet new MARPOL NO_x emissions standards under the severe sulfur exposure conditions experienced in marine diesel engines. Severe SCR performance degradation is observed specifically at low evaluation temperatures (< 250°C) for catalyst sulfated at 250 and 400°C, with the lower sulfur exposure temperature having the most negative impact. NO and NH₃ oxidation are only inhibited in the sulfated samples, suggesting the loss of access to the Cu sites active for oxidation over Cu-CHA due to the presence of sulfur. On the other hand, NH₃ storage increases in the presence of sulfur, which is likely due to the formation of ammonium sulfate at evaluation temperatures below 300°C. The similarity in NO_x reduction performance of fresh, desulfated, and sulfated catalysts at temperatures above 300°C is apparently due to the decomposition of ammonium sulfate at 280°C. The deactivation of sulfur exposed Cu-CHA SCR catalysts, however, can be reversed by performing desulfation at temperatures as low as 500°C.

EPMA analysis reveals that the washcoat in sulfated samples is saturated from catalyst inlet to exit, with an even distribution of sulfur throughout the washcoat, while ICP-OES measurements found elevated levels of sulfur in all but the de-greened SCR catalyst and the catalyst desulfated for 30 minutes at 600°C. BET measurements with N₂ reveal that the presence of sulfur results in a 20% decrease in measured surface area and pore volume, but these losses can be recovered with desulfation under lean conditions. NH₃ absorption spectra obtained through DRIFTS were unable to identify any clear difference between de-greened and sulfated samples. However, DRIFTS absorption spectra for NO show a definitive loss in peak intensity associated with NO_x/nitrate absorption and formation on the Cu-CHA washcoat, indicating a loss in the number of active Cu sites available to react with NO_x species as a result of sulfur exposure.

The low temperature SCR performance deactivation observed in the current study is attributed to both the formation of ammonium nitrate at temperatures below 250°C and the loss of active Cu sites in the catalyst due to the presence of sulfur. With regards to the viability of Cu-CHA for marine diesel applications, as long as desulfation is carried out at temperatures above 500°C for at least 30 minutes, and the exhaust temperature is maintained above 250°C, the Cu-CHA SCR catalyst should achieve adequate NO_x conversion to meet MARPOL NO_x emission standards.

Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office. The authors gratefully acknowledge the support and guidance of program manager Kevin Stork at DOE.

Disclaimer

This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

References

- [1] J. Kwak, R. Tonkyn, D. Kim, J. Szanyi and C. Peden, *J. Catal.* 275 (2010) 187-190.
- [2] D. Fickel, E. D'Addio, J. Lauterbach and R. Lob, *Appl. Catal. B: Environ.* 102 (2011) 441-448.
- [3] S. Korhonen, D. Fickel, R. Lobo, B. Weckhuysen and A. Beale, *Chem. Commun.* 47 (2010) 800-802.
- [4] S. Schmieg, S. Oh, C. Kim, D. Brown, J. Lee, C. Peden and D. Kim, *Catal. Today* 184 (2011) 252-261.
- [5] *Federal Register* Vol. 75, No. 83 (2010).
- [6] I. Nam, S. Choo, D. Koh and Y. Kim, *Catal. Today* 38 (1997) 181-186.
- [7] A. Plomares, J. Prato and A. Corma, *Catal. Today* 75 (2002) 367-371.
- [8] Y. Cheng, C. Montreuil, G. Cavataio and C. Lambert, *SAE Technical Paper Series* 2009-01-0898.
- [9] Y. Cheng, C. Montreuil, G. Cavataio and C. Lambert, *SAE Technical Paper Series* 2008-01-1023.
- [10] B. Ramachandran, R. Herman, S. Choi, H. Stenger, C. Lyman and J. Sale, *Catal. Today* 55 (200) 281.
- [11] J. Theis, *SAE Technical Paper Series* 2009-01-0900.
- [12] Y. Cheng, C. Lambert, J. K. D.H. Kim, S. Cho and C. Peden, *Catal. Today* 151 (2010) 266-270.
- [13] L. Zhang, D. Wang, Y. Liu, K. Kamasamudram, J. Li and W. Epling, *Appl. Catal. B: Environ.* 156-157 (2014) 371-377.
- [14] A. Kumar, M. Smith, K. Kamasamudram, N. Currier, H. An and A. Yezerets, *Catal. Today* 231 (2014) 75-82.
- [15] G. Caiazzo, G. Langella, F. Miccio and F. Scala, *XXXV Meeting of the Italian Section of the Combustion Institute* (2012).
- [16] *Symposium Proceedings of International Symposium on Marine Engineering and Technology*, London, May 13-17, 2013.
- [17] G. Zheng, A. Kotrba, M. Golin, T. Gardner and A. Wang, *SAE Technical Paper Series* 2012-01-1960.
- [18] L. Xie, F. Liu, K. Liu, X. Shi and H. He, *Catal. Sci. Technol.* 4 (2014) 1104-1110.

- [19] K. Wijayanti, S. Andonova, A. Kumar, J. Li, K. Kamasamudram, N. W. Currier, A. Yezerets and L. Olsson, *Appl. Catal. B: Environ* 166-167 (2015) 568-579.
- [20] D. W. Brookshear, K. Nguyen, T. J. Toops, B. G. Bunting and W. F. Rohr, *Top. Catal.* 55 (2012) 62-67.
- [21] M. Ruggeri, I. Nova, E. Tronconi, J. Pihl, T. Toops and W. Partridge, *Appl. Catal. B: Environ.* (2014) 181-192.
- [22] H. Sjoval, E. Fridell, R. J. Blint and L. Olsson, *Top. Catal.* 42-43 (2007) 180-188.
- [23] N. Wilken, K. Wijayanti, K. Kamasamudram, N. W. Currier, R. Vedaiyan, A. Yezerets and L. Olsson, *Appl. Catal. B: Environ.* 111-112 (2011) 58-66.
- [24] L. Ma, Y. Cheng, G. Cavataio, R. W. McCabe, L. Fu and J. Li, *Appl. Catal. B: Environ.* 156-157 (2014) 428-437.
- [25] D. Wang, L. Zhang, K. Kamasamudram and W. S. Epling, *ACS Catal.* 3 (2013) 871-881.
- [26] B. Ramachandran, R. G. Herman, S. Choi, H. G. Stenger, C. E. Lyman and J. W. Sale, *Catal. Today* 55 (2000) 281-290.
- [27] F. Yin, A. L. Blumenfeld, V. Gruver and J. J. Fripiat, *J. Phys. Chem. B* 101 (1997) 1824-1830.
- [28] H. Zhu, J. H. Kwak, C. H. F. Peden and J. Szani, *Catal. Today* 205 (2013) 16-23.
- [29] H. Sjoval, E. Fridell, R. J. Blint and L. Olsson, *Top. Catal.* 113-117 (2007) 42-43.
- [30] A. Zecchina, L. Marchese, S. Bordiga, C. Paze and E. Gianotti, *J. Phys. Chem. B.* 101 (1997) 10128-10135.
- [31] D. Klukowski, P. Balle, B. Geiger, S. Wagloehner, S. Kureti, B. Kimmerle, A. Bailer and J. D. Grunwaldt, *Appl. Catal. B: Environ.* 93 (2009) 185-193.
- [32] G. Chen, J. Gao, Q. Du, X. Fu, Y. Yin and Y. Qin, *Ind. Eng. Chem. Res.* 49 (2010) 12140-12147.
- [33] L. Zhang, J. Pierce, V. L. Leung, D. Wang and W. S. Epling, *J. Phys. Chem. C.* 117 (2013) 8282-8289.
- [34] K. I. Hadjiivanov, *Catal. Rev. Sci. Eng.* 42 (2000) 71-144.
- [35] R. Q. Long and R. T. Yang, *J. Catal.* 207 (2002) 224-231.
- [36] J. Szanyi, J. Kwak, H. Zhu and C. Peden, *Phys. Chem. Chem. Phys.* 15:7 (2013) 2368-2380.

Table 1. Allowable Sulfur Content of Fuel for Marine Diesel Engines [3]

Date	Sulfur Limit in Fuel (%m/m)	
	SO _x Emissions Control Area	Global
2000	1.5%	4.5%
2010.07	1.0%	
2012		3.5%
2015		
2020*	0.1%	
* - alternative date is 2025, to be decided by a review in 2018		

Table 2. NO_x Emissions Limits for Marine Diesel Engines (n = engine speed in revolutions per minute) [3]

Tier	Date	NO _x Limit, g/kWh		
		n < 130	130 ≤ n < 2000	n ≥ 2000
Tier I	2000	17.0	$45 \cdot n^{-0.2}$	9.8
Tier II	2011	14.4	$44 \cdot n^{-0.23}$	7.7
Tier III*	2016*	3.4	$9 \cdot n^{-0.2}$	1.96
* in NO _x Emissions Control Areas only				

Table 3. Example Engine Data for Large Marine Diesel Engine [16]

Ambient and gaseous emission data from manufacturer engine					
Mode	-	1	2	3	4
Engine Power	%				
	kW	31640.0	23730.0	51820.0	7910.0
Engine Load	%	100	91	80	63
Engine Speed	rpm	80.0	80.0	80.0	80.0
Exhaust gases					
Exh. Gas temp. (after T/C)	°C	281.0	225.3	252.3	258.7
Gaseous Emission Data					
CO (Dry)	ppm	47.0	51.0	115.0	327.0
CO ₂ (Dry)	%	4.28	3.85	3.59	3.39
HC (Wet)	ppmC	59.0	60.5	50.0	46.5
O ₂ (Dry)	%	15.05	15.70	16.00	16.40
NOx	ppm	878	818	736	688
NOx Specific	g/kWh	12.53	12.06	12.39	12.40

Figure 1. Impact of desulfation on standard SCR performance of cores aged at 250°C.

Figure 2. Standard SCR performance of sulfated and desulfated catalysts.

Figure 3. Fast SCR performance of sulfated and desulfated catalysts.

Figure 4. NH₃ oxidation over sulfated and desulfated catalysts.

Figure 5. NH₃ storage in sulfated and desulfated catalysts.

Figure 6. Sulfur micrographs of fresh Cu-CHA SCR with backscatter images (BSE).

Figure 7. Sulfur micrographs at inlet and exit of Cu-CHA SCR sulfated for two hours at 250°C with backscatter images (BSE).

Figure 8. Sulfur micrographs at inlet and exit of Cu-CHA SCR sulfated for two hours at 400°C with backscatter images (BSE).

Figure 9. Line scans of sulfur in sulfated Cu-CHA SCR catalysts.

Figure 10. ICP-OES measurements of sulfur in sulfated and desulfated Cu-CHA SCR catalysts.

Figure 11. BET surface area measurements of de-greened, sulfated, and desulfated Cu-CHA SCR catalysts.

Figure 12. BET surface area measurements of de-greened, sulfated, and desulfated Cu-CHA SCR catalysts.

Figure 13. DRIFTS absorbance spectra of NO + O₂ on de-greened, sulfated, and desulfated Cu-CHA SCR catalysts (1800-1450 cm⁻¹).

Figure 14. DRIFTS absorbance spectra of NO + O₂ on de-greened, sulfated, and desulfated Cu-CHA SCR catalysts (2300-2100 cm⁻¹).