OZONE OXIDATION OF SOLID DEPOSITS PRODUCED BY THE THERMAL STRESSING OF JET FUEL

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Introduction

Jet fuel serves as a coolant in military aircraft and it is exposed to higher temperatures before it is burned in the advanced aircraft because of increasing thermal loads. High thermal loads can lead to temperatures as high as 500°C on metal surfaces in the fuel delivery system. Exposure to such high temperatures accelerates the reactions of hydrocarbons and heteroatom species in jet fuel and results in the formation of carbonaceous deposits on metal surfaces. Rapid accumulation of solid deposits on various components of the fuel system, including valves, flow tubes, and nozzles would cause a catastrophic failure of the aircraft engine [1,2].

Temperature Programmed Oxidation (TPO) can be used to characterize the carbon deposits produced by the thermal stressing of jet fuel over various catalytic and non-catalytic substrates. Such characterization is based on the oxidation reactivity of the deposits, which is closely related to their structural morphology[2]. The high temperature and catalytic activity of the substrate may however produce some highly ordered deposits that are artifacts of the TPO analysis. To eliminate the possible complications with analyzing the carbon deposits at high temperatures, deposited substrates can be oxidized with ozone at low temperatures. A rationale for this approach is that ozone (O_3) has a strong oxidation capacity that can be attributed to its ability to form nascent oxygen or free oxygen radicals. This reactive species reacts with different types of carbon samples even at room temperature[3,4]. Thus it can be used for cleaning carbon deposited catalytic and non-catalytic surfaces through oxidation below 200 °C [3].

This study compares the characterization of carbon deposits produced from the thermal stressing of jet fuel by TPO of ozone oxidized samples to characterization by TPO alone.

Experimental

Thermal stressing experiments were carried out at super-critical conditions of 480 °C and 500 psig[1,5] in an isothermal, glass lined flow reactor of OD 1/4". The carbon deposits were collected over 13 cm X 3mm coupons of Ni; Fe/Ni- (55/45); Inconel 600 (composition wt%- Ni:72%, Fe:8%, Cr:15.5%, Mn: 1.0%, Cu:5000ppm, C:1500 ppm, Si:5000 ppm, S:150ppm)[6] stressed with JP-8 (military jet fuel) for 5, 5 and 2 hours respectively; SS321 (composition wt% is Ni:10.5%, Fe:68%, Cr:18%, Mn: 2.0%, C: 0.08%, Si:1%, S:10.03ppm, Ti: 0.6%) stressed with Jet A (commercial aviation) for 24 hours. and SS321 stressed with JP-8 (military jet fuel) for 24 hours respectively. The deposit morphology was studied using Scanning electron Microscopy (SEM) and characterized by TPO in a LECO Multiphase Carbon Analyzer and oxidation with ozone in a reactor connected to a UNIZONE™ LOX Praxair-Trailigaz Ozone generator. The carbon deposited samples were cut into 5cm coupons for the ozone analyses and placed in a quartz boat inside a reactor. During the analysis the sample was exposed to an ozone stream flowing at a rate of 250cc/min at a constant reaction temperature of 150°C. Ozone was produced by converting UHP Molecular oxygen in an ozonator using high voltage at about 19,000V and a conversion efficiency of about 3%. The concentration of the product gases were analyzed using a mass spectrometer and an IR detector. Following ozone oxidation, the samples were again characterized by TPO in the carbon analyzer.

Results and Discussion

As seen in Figure 1, the SEM images and TPO profile of the deposits produced by JP-8 stressed over Ni for 5 hours, suggest that solid deposits of varying oxidation reactivities are produced due to the high catalytic activity of Ni for dehydrogenation[5]. The SEM images show a significant decrease in the amorphous deposits formed over the nickel-sulfide crystals after oxidation using ozone. Comparing the TPO profiles of the sample, shows that the amount of ordered carbon deposits is nearly the same before and after ozone oxidation while most of the reactive deposits have been oxidized.

Figure 2 compares the SEM images and TPO profiles, before and after ozone oxidation of the carbon deposits produced by stressing JP-8 over Fe-Ni (55/45) for 5 hours. The SEM images clearly suggest oxidation, caused by a decrease in the amount of deposits and an increase in void spaces over the metal surface. A comparison of the TPO profiles of this sample before and after ozone oxidation shows that the latter oxidizes almost all the deposits present on the surface except leaving behind a small amount of the highly ordered species oxidizing around 780 °C. This maybe due to the significant Fe content in the substrate that shows high catalytic activity during carbon oxidation.

The thermal stressing of JP-8 over Inconel 600 for 2 hours produces only about 20 μg/cm^2 of carbon deposits, most of which are less ordered in nature as shown in the SEM images of Figure 3. Since considerably less deposits are produced over this sample, the difference in amount of deposits before and after ozone oxidation are not clearly revealed by SEM. As can be seen in the TPO profile of the deposits after ozone oxidation, the intensities of the low temperature and high temperature CO_2 evolution peaks is nearly the same. However the decrease in intensity of the high temperature peak, before and after ozone oxidation is about 1/4 of the decrease in intensity of the low temperature CO_2 evolution peak. The large split in the low temperature CO_2 evolution peaks after ozone oxidation suggests that TPO reflects the different types of deposits on the surface more distinctly with removal of some of the more reactive species.

Comparing the SEM images in Figure 4, we can see that the amorphous deposits produced by thermally stressing Jet A over the SS321 surface for 24 hours have been removed by ozone oxidation revealing the underlying layers of more ordered deposits, metal and metal sulfide crystals. The total carbon amount on the original carbon deposited sample is about 52 μg/cm^2. Ozone oxidation removes about 33 μg/cm^2 of solid deposits over the surface. The TPO profile of this sample also shows that the intensity of the peak at around 350 °C is almost eliminated after ozone oxidation whereas the intensities of the high temperature CO_2 peaks at around 550 °C and 580 °C respectively following ozone oxidation is greater than 50% of the original TPO profile. Since the profile of high temperature CO_2 peaks is nearly unaltered after a significant decrease in the low temperature CO_2 peaks, this suggests that the ordered carbon deposits are produced from thermal stressing and not as an artifact of the TPO analysis.

The CO_2 evolution profile during ozone oxidation, as recorded by a mass spectrometer connected to the output of the reactor suggested the presence of at least two types of carbon deposits over the samples since the rate of reaction initially increased during oxidation of the more reactive species or amorphous carbon deposits, then decreased as most of the less ordered carbon had been removed. At low temperatures the activation energy of the reaction isn't sufficient for the oxidation of the less reactive deposits even by ozone.

Any further increase in the temperature of the reaction caused decomposition of the ozone to molecular oxygen, which was undesirable. The difference in weight between a completely oxidized sample (after TPO) and an ozone oxidized sample confirmed the presence of remaining carbon deposition on the substrate after ozone oxidation.

Exposure to ozone removed about 90% amorphous carbon deposits at 150 ˚C. This temperature during ozone oxidation is very low to cause any structural changes through any thermal or catalytic reactions. The SEM images as shown in Figures 1-5 following ozone oxidation revealed some of the more ordered carbon structures. A very small, low temperature CO_2 peak but a significant high temperature CO_2 evolution peak during temperature programmed oxidation of the ozone-oxidized samples suggests that the less reactive carbonaceous deposits were formed on the substrate during thermal stressing of the jet fuel and not from secondary pyrolysis of the more reactive deposits during TPO as speculated.

The intensity of the high temperature CO_2 peaks in most of the ozone oxidized samples was lower than that of the original carbon deposited sample. This is probably due to the high reactivity of ozone, which along with the amorphous carbon may oxidize some of the more ordered structures. The temperature of CO_2 evolution of the less reactive carbon deposits following ozone oxidation was the same as that of the original TPO profile as shown in Figures 1, 2, 3, 4.

In Figure 5, however, the temperature of peak CO_2 evolution from oxidation of the ordered carbon deposits increased by 120 ˚C after removal of the amorphous carbon deposits by ozone. This may be due to the fact that, in the original sample containing carbonaceous deposits of variant oxidation reactivities, the heat released by the oxidation of the amorphous carbon deposits and associated hydrogen increased the temperature of the sample to about 583 ˚C while the temperature recorded by the furnace was still 462 ˚C, causing an apparent lowering of oxidation temperature of the ordered carbon deposits.

Another possibility for the shift of the high temperature CO_2 peak in Figure 5 could be oxidative coupling of the molecules in the carbonaceous deposits due to the interaction of the decomposed ozone species with the deposits during ozone oxidation. The decomposed ozonide can form hydroxyl, carbonyl and –C-O- surface moieties on the deposit[7].

Conclusions

The presence of a high temperature CO_2 peak after removal of most of the amorphous carbon deposits from the substrate is strong evidence that the highly ordered carbon deposits on the sample surface are created during thermal stressing and not produced as an artifact during the characterization of the samples during TPO.

Although the degree of oxidation by ozone may be inferior to that by a pure O_2 stream it is less energy intensive and the low temperatures can prolong substrate life[8].

Acknowledgement. We are grateful for financial support from the U.S. Air Force Office of Scientific Research.

References

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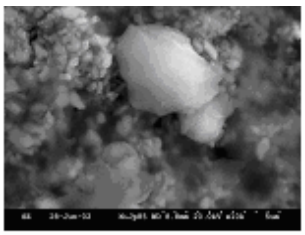
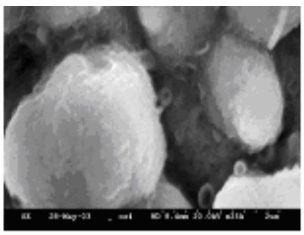
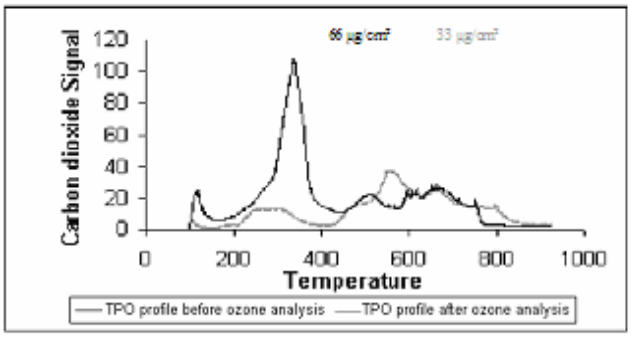


(a) - After thermal stressing

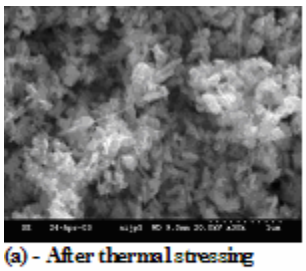


(b) - After Ozone oxidation

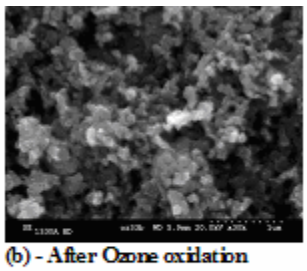


(c)

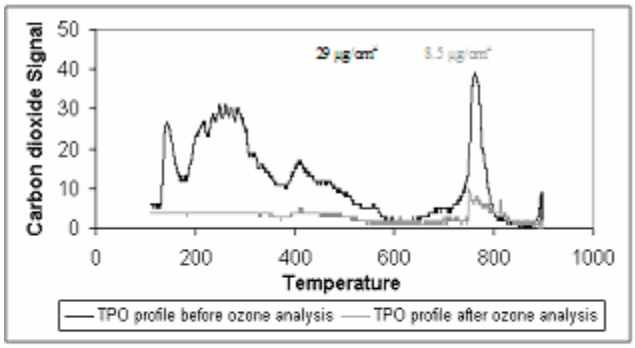
Figure 1: Comparsion of SEM images and TPO profiles of the carbon deposits produc from JP-8 stressed over Ni for 5 hours before and after ozone oxidation



(a) - After thermal stressing

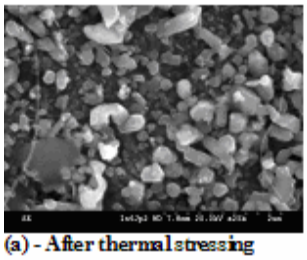


(b) - After Ozone oxidation

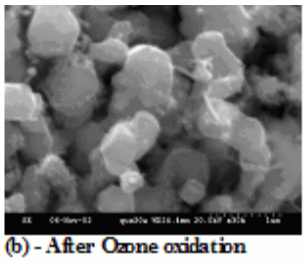


(c)

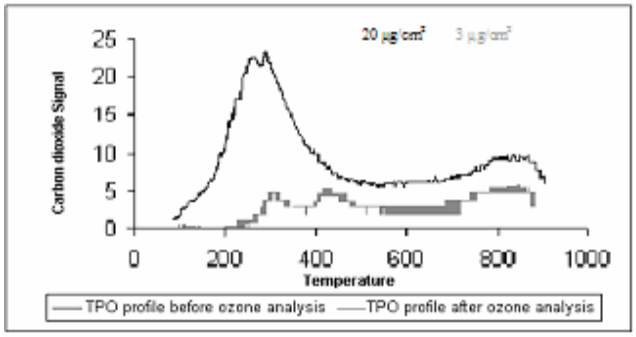
Figure 2: Comparison of SEM images and TPO profiles of carbon deposits formed from JP-8 stressed over Fe/Ni- 55/45 for 5 hours before and after ozone oxidation



(a) - After thermal stressing

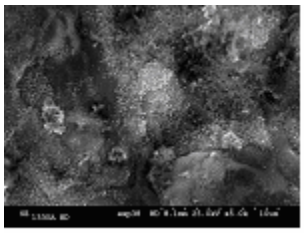


(b) - After Ozone oxidation

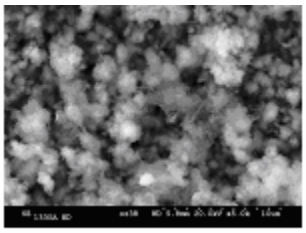


(c)

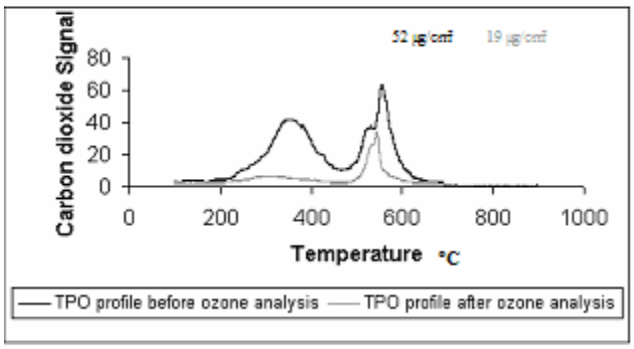
Figure 3: Comparison of SEM images and TPO profiles of carbon deposits produced from JP-8 stressed over Inconel 600 for 2 hours before and after ozone oxidation



(a) - After thermal stressing

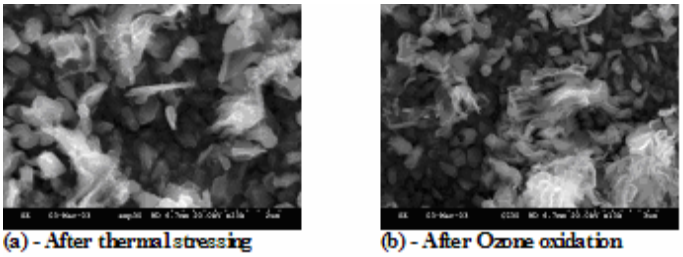


(b) - After Ozone oxidation

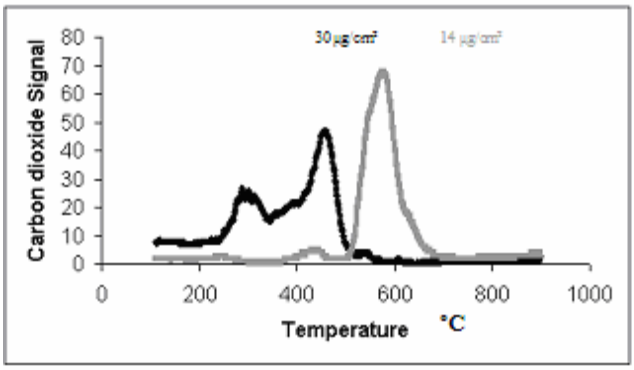


(c)

Figure 4: Comparison of the SEM images and TPO profiles of carbon deposits produced from Jet A stressed over SS321 for 24 hours, before and after ozone oxidation



(a) - After thermal stressing (b) - After Ozone oxidation



(c)

Figure 5: Comparison of SEM images and TPO profiles of carbon deposits produced from JP-8 stressed over SS321 for 24 hours before and after ozone oxidation