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FATE OF SO_2 DURING PLASMA TREATMENT OF DIESEL ENGINE EXHAUST

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Abstract

Several catalytic aftertreatment technologies rely on the conversion of NO to NO_2 to achieve efficient reduction of NO_x and particulates in diesel engine exhaust. These technologies require low sulfur fuel because the catalyst component that is active in converting NO to NO_2 is also active in converting SO_2 to SO_3. A non-thermal plasma can be used for the selective partial oxidation of NO to NO_2 in the gas-phase under diesel engine exhaust conditions. This paper discusses how a non-thermal plasma can efficiently oxidize NO to NO_2 without oxidizing SO_2 to SO_3. It is shown that the presence of hydrocarbons in the plasma is essential for enhancing the selective partial oxidation of NO and suppressing the oxidation of SO_2.

Introduction

NO_2 plays an important role in several aftertreatment technologies. In selective catalytic reduction (SCR) with hydrocarbons, many studies suggest that the conversion of NO to NO_2 is an important intermediate step in the reduction of NO_x to N_2 [ref. 1-3]. In lean-NO_x traps, the catalytic oxidation of NO to NO_2 on precious metals is followed by the formation of a nitrate on alkali or alkaline earth metal oxides [ref. 4-6]. In continuously regenerated particulate traps (CRT), a precious metal catalyst is used to oxidize NO to NO_2 upstream of a particulate filter; the NO_2 is then utilized to oxidize the carbon fraction of the trapped particulates [ref. 7-8].

The SCR, lean-NO_x trap and CRT technologies require low sulfur fuel because the catalyst component that is active in converting NO to NO_2 is also active in converting SO_2 to SO_3. The SO_3 leads to the formation of sulfuric acid and sulfates that increase the particulates in the exhaust and/or poison the active sites on the catalyst.

A non-thermal plasma can be used for the selective partial oxidation of NO to NO_2 in the gas-phase under diesel engine exhaust conditions [ref. 9-10]. The sulfur tolerance of several aftertreatment technologies can be substantially improved if it can be shown that a non-thermal plasma is more selective towards the oxidation of NO compared to the oxidation of SO_2.

This paper discusses how a non-thermal plasma can efficiently oxidize NO to NO_2 without oxidizing SO_2 to SO_3.

Results

Chemical kinetics calculations and experimental data are presented here to quantify the NO and SO_2 oxidation in the plasma for gas mixtures containing various levels of NO, SO_2, O_2, H_2O and hydrocarbons. The plasma reactor used in our experiments is a pulsed corona discharge reactor consisting of a metal wire inside a metal cylinder. Although we have used a pulsed corona plasma reactor, the plasma chemistry is not peculiar to this type of plasma processor. All electrical discharge plasma reactors accomplish essentially the same gas-phase plasma chemistry under the same gas conditions [ref. 11]. FTIR is the characterization method we have used to study the oxidation of SO_2.

Six gas mixtures containing various levels of NO, SO_2, O_2, H_2O and hydrocarbons at a gas temperature of 260°C were studied. The mixtures studied were:

Gas Mixture (I): 10% O_2, 500 ppm SO_2, balance N_2

Gas Mixture (II): 10% O_2, 500 ppm SO_2, 500 ppm NO, balance N_2

Gas Mixture (III): 10% O_2, 500 ppm SO_2, 1000 ppm C_3H_6, balance N_2

Gas Mixture (IV): 10% O_2, 500 ppm SO_2, 500 ppm NO, 1000 ppm C_3H_6, balance N_2

Gas Mixture (V): 10% O_2, 5% H_2O, 500 ppm SO_2, balance N_2

Gas Mixture (VI): 10% O_2, 5% H_2O, 500 ppm SO_2, 1000 ppm C_3H_6, balance N_2

The experiments used a large quantity of SO_2 and a significant plasma power level. The level of plasma power applied corresponds to an average energy density of 40 J/L, which would correspond to around 4% of the engine output power. If no oxidation effect is discovered using these reaction conditions, then it is not likely that milder conditions will present a different outcome, so this can be considered a worst case scenario.

Results on Gas Mixture (I)

The purpose of studying gas mixture (I) is to quantify the amount of SO_2 oxidation by the O radical. Electron-impact dissociation of O_2 in the plasma produces O radicals:

$$e + O_2 \rightarrow e + O(^3P) + O(^3P, ^1D) \quad (1)$$

where $O(^3P)$ (simply referred to as O) and $O(^1D)$ are ground-state and metastable excited-state oxygen atoms, respectively. In the absence of water vapor, most of the $O(^1D)$ relax to the ground state O. The O radical could oxidize SO_2:

$$O + SO_2 + M \rightarrow SO_3 + M \quad (2)$$

where M is a third molecule such as N_2 or O_2. Ozone could also be formed:

$$O + O_2 + M \rightarrow O_3 + M \quad (3)$$

and the ozone could then oxidize SO_2:

$$O_3 + SO_2 \rightarrow SO_3 + O_2 \quad (4)$$

Figure 1(a) shows chemical kinetics calculations of the concentrations of species during plasma processing of gas mixture (I). The species concentrations are presented as a function of the electrical energy density in the plasma. The most noticeable product is ozone. Most of the O radicals are consumed in the production of ozone according to reaction (3). At high energy densities, the plasma produces NO, which is then immediately oxidized to NO_2. A small amount of NO is produced by the plasma:

$$N + O_2 \rightarrow NO + O \quad (5)$$

The ozone is then consumed in the oxidation of NO to NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (6)$$

The amount of SO_2 oxidation by ozone is relatively small. The SO_2 is oxidized to SO_3 directly by the O radical according to reaction (2).

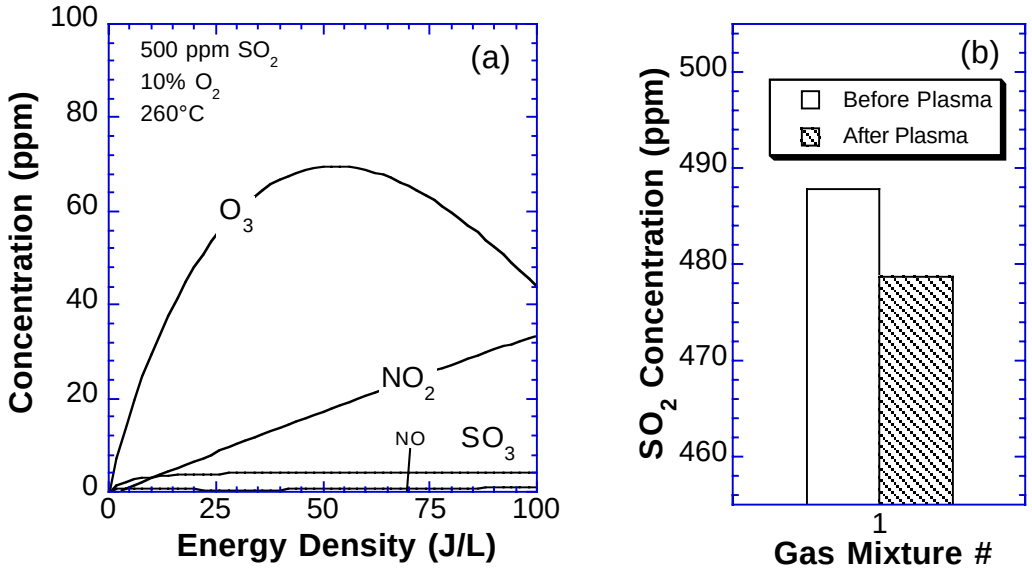

Figure 1. (a) Chemical kinetics calculation of the concentrations of species during plasma processing of 500 ppm SO_2 in 10% O_2, balance N_2 at 260°C. (b) FTIR measurements of the SO_2 concentration before and after plasma processing (energy density of 40 J/L) of the same mixture.

The O radicals also reduce NO_2 and SO_3 back to NO and SO_2, respectively:

$$O + NO_2 \rightarrow NO + O_2 \quad (7)$$

$$O + SO_3 + M \rightarrow SO_2 + O_2 + M \quad (8)$$

The backconversion of SO_3 to SO_2 accounts for the small amount of SO_3 that is formed in the plasma. The amount of SO_3 produced is less than 10 ppm.

Figure 1(b) shows the FTIR measurements of the SO_2 concentration before and after plasma processing of gas mixture (I). The energy density applied to plasma in the experiment is 40 J/L. The amount of SO_2 oxidized in gas mixture (I) is of the order of 9 ± 2 ppm.

Results on Gas Mixture (II)

The purpose of using gas mixture (II) is to study the competition between the oxidation of NO and the oxidation of SO_2 by the O radical. In gas mixture (II) the O radicals can also be consumed in the oxidation of NO via ozone according to reaction (6) and by direction oxidation of NO by the O radical:

$$O + NO + M \rightarrow NO_2 + M \qquad (9)$$

Figure 2(a) shows chemical kinetics calculations of the concentrations of species during plasma processing of gas mixture (II). Ozone is no longer detectable. Any ozone produced by the plasma is quickly consumed in the oxidation of NO to NO_2. A large amount of O radicals is also consumed in the oxidation of NO to NO_2. However, the efficiency for oxidation of NO to NO_2 is very low because the O radicals backconvert NO_2 to NO according to reaction (7). Even at high energy density, the maximum oxidation of NO to NO_2 is only 10%.

SO_3 formation in gas mixture (II) remains low because the oxidation of SO_2 to SO_3 is counterbalanced by reduction of SO_3 to SO_2 according to reaction (8). The amount of SO_3 formed in gas mixture (II) is less that that in gas mixture (I) because most of the O radicals are consumed in the oxidation-reduction reactions involving NO_x.

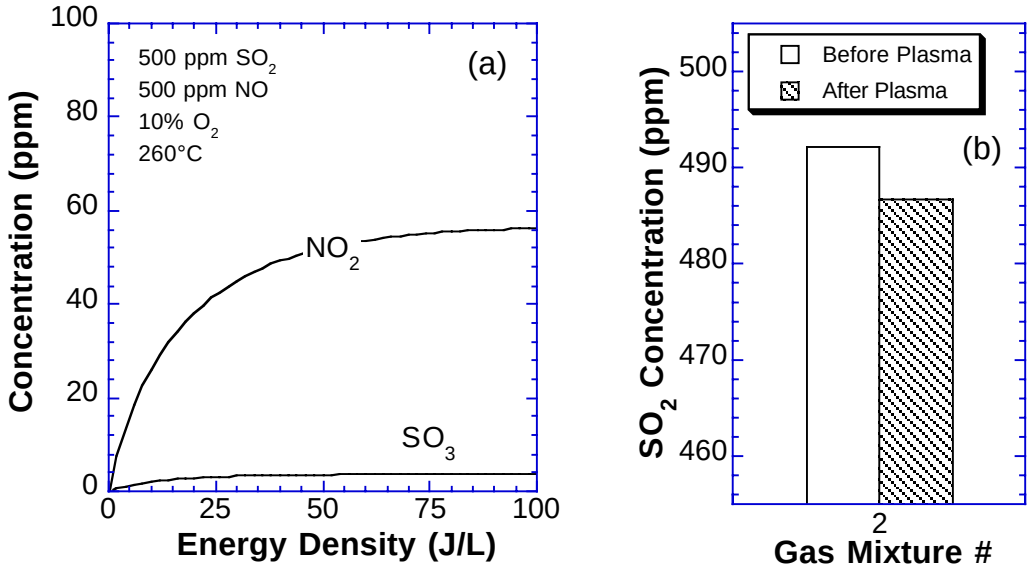

Figure 2. (a) Chemical kinetics calculation of the concentrations of species during plasma processing of 500 ppm SO_2, 500 ppm NO in 10% O_2, balance N_2 at 260°C. (b) FTIR measurements of the SO_2 concentration before and after plasma processing (energy density of 40 J/L) of the same mixture.

Figure 2(b) shows the FTIR measurements of the SO_2 concentration before and after plasma processing of gas mixture (II). The amount of oxidation of SO_2 in gas mixture (II) less compared to that in gas mxiture (I) because of the presence of NO. This is expected because the O radicals are consumed in the oxidation of NO. The amount of SO_2 oxidized in gas mixture (II) is less than 6 ppm.

Results on Gas Mixture (III)

The purpose of studying gas mixture (III) is to examine the competition between the oxidation of SO_2 and the oxidation of C_3H_6 by the O radical:

$$O + C_3H_6 \rightarrow \text{products} \qquad (10)$$

The rate constants for the $O + C_3H_6$ reactions are much larger than that for the $O + SO_2$ reaction. It is therefore expected that most of the O radicals will be scavenged by C_3H_6, and the level of SO_2 oxidation will be greatly decreased.

Figure 3(a) shows chemical kinetics calculations of the concentrations of species during plasma processing of gas mixture (III). A small amount of NO is produced by the plasma according to reaction (5). Some of the O radicals are consumed in converting any NO that is produced in the plasma to NO_2 according to reactions (6) and (9). Most of the O radicals are consumed in reactions with C_3H_6 according to reaction (10). SO_3 formation is very low because most of the O radicals are scavenged by C_3H_6.

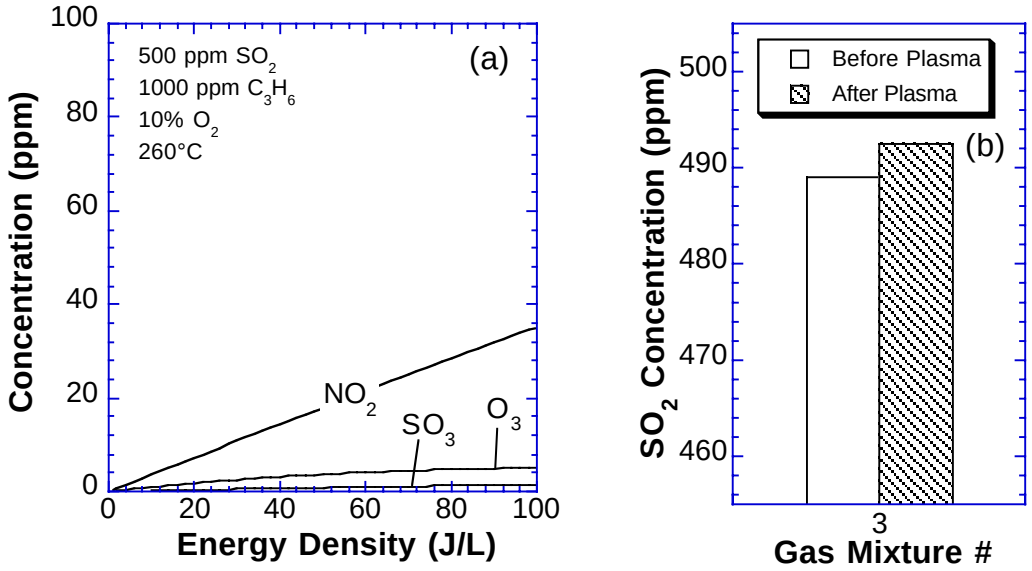

Figure 3. (a) Chemical kinetics calculation of the concentrations of species during plasma processing of 500 ppm SO_2, 1000 ppm C_3H_6 in 10% O_2, balance N_2 at 260°C. (b) FTIR measurements of the SO_2 concentration before and after plasma processing (energy density of 40 J/L) of the same mixture.

Figure 3(b) shows the FTIR measurements of the SO_2 concentration before and after plasma processing of gas mixture (III). Gas mixture (III) contains a hydrocarbon. As a result, the plasma reaction produces

water vapor from the hydrocarbon oxidation that interferes slightly with the FTIR measurement. It is possible to use the IR absorbance at a different wavelength; however, the data suffers from more variability. Nevertheless, there is no detectable decrease in SO_2, as expected, because the O radicals are scavenged by the hydrocarbon.

Results on Gas Mixture (IV)

The purpose of studying gas mixture (IV) is to examine the effect of C_3H_6 on both the oxidation of NO and the oxidation of SO_2. Whereas the hydrocarbon diminishes the oxidation of SO_2, the hydrocarbon greatly enhances the oxidation of NO to NO_2.

The effect of C_3H_6 on both the oxidation of NO and the oxidation of SO_2 is shown in Figure 4(a). The hydrocarbon greatly enhances the plasma oxidation of NO to NO_2, whereas the oxidation of SO_2 remains at a very low level. The level of SO_2 oxidation in mixture (IV) is slightly larger compared to that in gas mixture (III). This is because the hydrocarbon-enhanced oxidation of NO to NO_2 is accompanied by the production of OH radicals. In the presence of hydrocarbons, the NO is mainly oxidized to NO_2 by

$$NO + HO_2 \rightarrow NO_2 + OH \quad (11)$$

$$NO + ROO \rightarrow NO_2 + RO \quad (12)$$

where R is a hydrocarbon radical. The hydrocarbons lower the energy cost for the oxidation of NO by converting O to HO_2; the OH radical is then reproduced when NO is oxidized by HO_2. This cyclic process leads to a very efficient utilization of the plasma-produced O radicals and minimizes the electrical energy required for the oxidation of NO to NO_2.

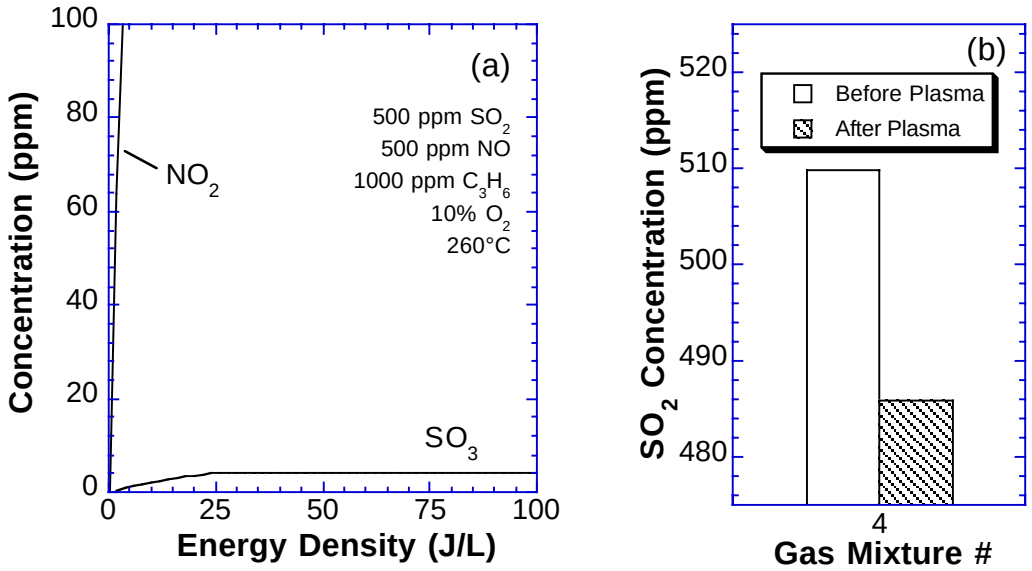

Figure 4. (a) Chemical kinetics calculation of the concentrations of species during plasma processing of 500 ppm SO_2, 500 ppm NO, 1000 ppm C_3H_6 in 10% O_2, balance N_2 at 260°C. (b) FTIR measurements of the SO_2 concentration before and after plasma processing (energy density of 40 J/L) of the same mixture.

The OH radicals produced by reaction (11) can oxidize SO_2:

$$OH + SO_2 + M \rightarrow HSO_3 + M \quad (13)$$

followed by HSO_3 reaction with O_2 to produce SO_3:

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \quad (14)$$

The rate constant for the OH + SO_2 reaction is much larger compared to that for the O + SO_2 reaction. The amount of H_2O produced by hydrocarbon oxidation in gas mixture (IV) is low enough so that SO_3 is not further converted to H_2SO_4.

Figure 4(b) shows the FTIR measurements of the SO_2 concentration before and after plasma processing of gas mixture (IV). The water vapor produced by hydrocarbon oxidation interferes with the FTIR measurement and the data suffers from more variability. The decrease in SO_2 for gas mixture (IV) is at the extreme edge of the 95% confidence limit for the experimental data taken with this mixture.

Results on Gas Mixture (V)

Diesel engine exhaust contains 5 to 10% H_2O. In the presence of H_2O, the metastable oxygen atom, $O(^1D)$, will react with H_2O to produce OH radicals:

$$O(^1D) + H_2O \rightarrow 2\ OH \quad (15)$$

Additional OH radicals could be produced directly from electron-impact dissociation of H_2O:

$$e + H_2O \rightarrow e + H + OH \quad (16)$$

The OH radical will oxidize SO_2 according to reaction (13), followed immediately by HSO_3 reaction with O_2 to produce SO_3 according to reaction (14). With percent levels of H_2O, the SO_3 will quickly form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (17)$$

The purpose of studying gas mixture (V) is to quantify the level of SO_2 oxidation by the OH radical. This is an important experiment because it is expected that the OH radical will be responsible for any significant plasma oxidation of SO_2 in diesel engine exhaust.

Figure 5(a) shows chemical kinetics calculations of the concentrations of species during plasma processing of gas mixture (V). In humid mixtures containing SO_2, plasma processing in the absence of hydrocarbons will produce large quantities of H_2SO_4. At an energy density of 40 J/L, the amount of H_2SO_4 formed in gas mixture (V) is calculated to be around 50 ppm.

Figure 5(b) shows the FTIR measurements of the SO_2 concentration before and after plasma processing of gas mixture (V). Because of the large amount of water vapor in this experiment, we rely on a different IR absorbance wavelength window and the water bands are subtracted from the sample spectra using a wet syn-air blank that does not have any SO_2 present. The after-plasma integrated absorbance is just

outside the 95% confidence interval. The amount of SO_2 oxidized in gas mixture (V) is measured to be about 35 ppm.

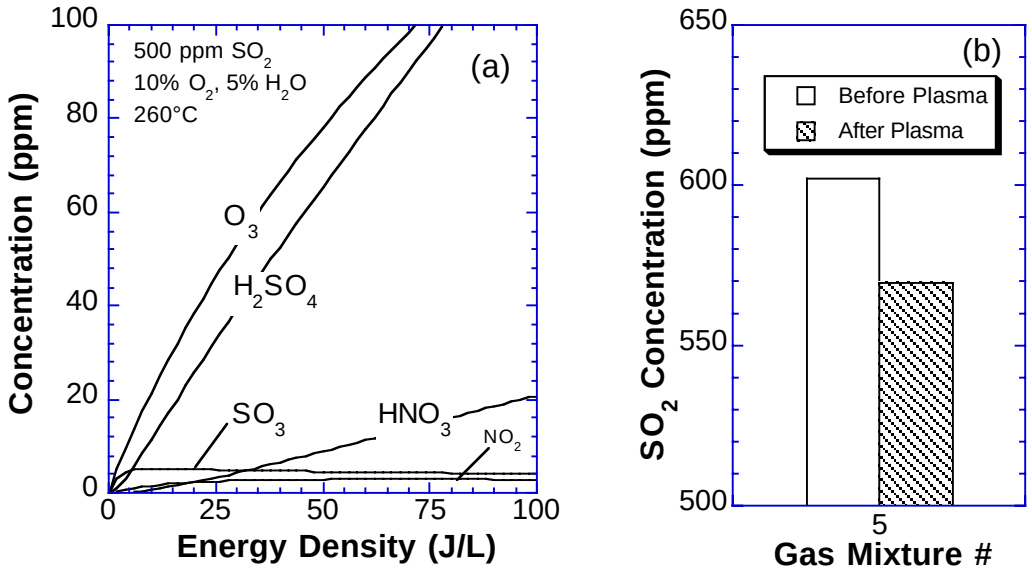

Figure 5. (a) Chemical kinetics calculation of the concentrations of species during plasma processing of 500 ppm SO_2 in 10% O_2, 5% H_2O, balance N_2 at 260°C. (b) FTIR measurements of the SO_2 concentration before and after plasma processing (energy density of 40 J/L) of the same mixture.

Results on Gas Mixture (VI)

The purpose of studying gas mixture (VI) is to examine the competition between the oxidation of SO_2 and the oxidation of C_3H_6 by the OH radical:

$$OH + C_3H_6 \rightarrow \text{products} \qquad (18)$$

The rate constants for the OH + C_3H_6 reactions are much larger than that for the OH + SO_2 reaction. It is therefore expected that most of the OH radicals will be scavenged by C_3H_6, and the level of SO_2 oxidation will be greatly decreased even in the presence of high levels of H_2O.

Figure 6(a) shows chemical kinetics calculations of the concentrations of species during plasma processing of gas mixture (VI). The O and OH radicals are consumed in reactions with C_3H_6. The oxidation of SO_2 is therefore suppressed.

Figure 6(b) shows the FTIR measurements of the SO_2 concentration before and after plasma processing of gas mixture (VI). The level of SO_2 apparently increases after the addition of plasma power. One possible explanation is the interference due to the water vapor produced by the hydrocarbon oxidation. Attempting to subtract the water spectrum due to hydrocarbon oxidation only increases the variance in the data set. Another possible reason for the absorbance increase in gas mixture (VI) after addition of plasma power is the formation of formaldehyde. It is known that formaldehyde is a major product of the partial oxidation of propene in a plasma. The hydrated form of formaldehyde could interfere with the IR absorbance measurement of SO_2. The experimental data for gas mixture (VI) remains inconclusive.

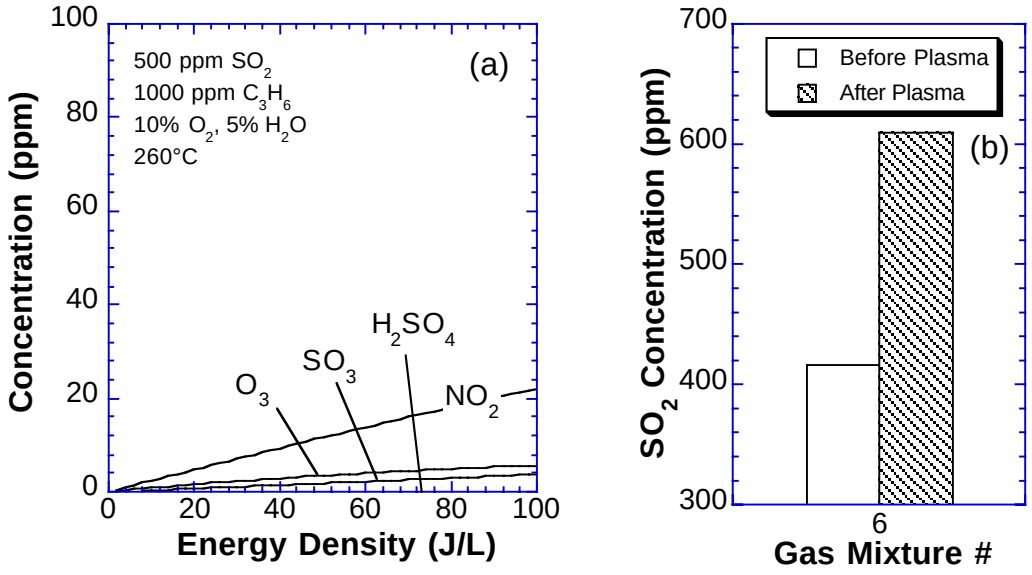

Figure 6. (a) Chemical kinetics calculation of the concentrations of species during plasma processing of 500 ppm SO_2, 1000 ppm C_3H_6 in 10% O_2, 5% H_2O, balance N_2 at 260°C. (b) FTIR measurements of the SO_2 concentration before and after plasma processing (energy density of 40 J/L) of the same mixture.

To understand what is happening in gas mixture (VI), we rely on a chemical kinetics model that has been validated by the experimental results on gas mixtures (I) to (V). The difficulty in explaining the results for gas mixture (VI) does not invalidate the results given for mixtures (I) to (V). The chemical kinetics calculations show that the SO_2 oxidation in mixture (VI) is suppressed by the hydrocarbon, as seen in Figure 6(a).

The chief difficulty in handling large amounts of water vapor stems from a diagnostic system that inadequately handles the interfering effects of water vapor. Systems can be built that more effectively deal with water vapor in the gas stream (e.g. the Perma Pure/Nafion membrane system, which we are bringing online). However, there are tradeoffs in understanding the effect of the membrane filter on the gas mixture. Although there are papers that address some of these concerns, it would still be necessary to investigate the effects of each constituent within the system and the overall performance of the system. This work is in progress.

Conclusions

The sulfur tolerance of several aftertreatment technologies can be substantially improved by using a non-thermal plasma for the selective partial oxidation of NO to NO_2. In a dry exhaust, the oxidation of SO_2 by the O radical is ineffective; thus there is no significant SO_3 formation. In the humid case that is typical of diesel exhaust, the OH radical can oxidize SO_2 to SO_3, which quickly gets converted to sulfuric acid. The presence of hydrocarbons in the plasma is essential for suppressing the oxidation of SO_2 and the formation of acids. The hydrocarbons in the plasma also play an important role in achieving high efficiency for oxidation of NO to NO_2 and minimizing the electrical power requirement in the plasma.

Acknowledgments

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