<table>
<thead>
<tr>
<th>Title</th>
<th>The combustion of carbon particulates using NO/O2 mixtures: The influence of SO4²⁻ and NOx trapping materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Authors(s)</td>
<td>Sullivan, James A.; Keane, Orla</td>
</tr>
<tr>
<td>Publication date</td>
<td>2006-05-30</td>
</tr>
<tr>
<td>Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Item record/more information</td>
<td><a href="http://hdl.handle.net/10197/3996">http://hdl.handle.net/10197/3996</a></td>
</tr>
<tr>
<td>Publisher's statement</td>
<td>This is the author's version of a work that was accepted for publication in Catalysis Today. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Catalysis Today, 114 (4) 2006-05, pp.340-345. DOI: 10.1016/j.cattod.2006.02.036</td>
</tr>
</tbody>
</table>

Downloaded 2018-12-27T23:41:34Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)

Some rights reserved. For more information, please see the item record link above.
The combustion of carbon particulates using NO/O₂ mixtures: The influence of SO₄²⁻ and NOₓ trapping materials.

James A Sullivan* and Orla Keane,
UCD School of Chemistry and Chemical Biology,
Dublin 4,
Ireland

Abstract

The activity of several catalysts are studied in the soot combustion reaction using Air and NO/Air as oxidising agents. Over Al₂O₃ supported catalysts NO(g) is a promoter for the combustion reaction with the extent of promotion depending on the Na loading. Over these catalysts SO₄²⁻ poisons this promotion by preventing NO oxidation through a site blocking mechanism. SiO₂ is unable to adsorb NO or catalyse its oxidation and over SiO₂ supported Na catalysts and NO(g) inhibits the combustion reaction. This is ascribed to a competition between NO and O₂. Over Fe ZSM-5 catalysts the presence of a NOₓ trapping component does not increase the combustion of soot in the presence of NO(g) and it is proposed that this previously reported effect is only seen under continuous NOₓ trap operation as NO₂ is periodically released during regeneration and thus available for soot combustion. Experiments during which the [NO]ₙ(g) is varied show that CO, rather than an adsorbed carbonyl-like intermediate, is formed upon reaction between NO₂ (the proposed oxygen carrier) and soot.

Keywords: Particulates, SiO₂, Al₂O₃, SO₄²⁻, Fe ZSM-5, NOₓ trap.

e-mail james.sullivan@ucd.ie, orla.keane@ucd.ie
**Introduction.**

Particulate matter is emitted from all combustion chambers [1]. It generally consists of carbonaceous material and may form around sulphate species which can act as nucleation sites for deposition [2]. They have a large variety of environmental and health impacts. Large particles are visible soot and contribute to the defacing of buildings and have also been implicated in global warming since they decrease the albedo of glacial ice floes and cause premature melting [3]. Smaller particles (<10 μm) can penetrate to the alveoli of the lung and lodge there. Polycyclic Aromatic Hydrocarbon species on the surface of the particulates can then cause cancer and other lung ailments [4].

One possible technique for the removal of these species involves trapping them within a ceramic monolith and subsequently oxidising them using O₂ and/or NO/O₂ mixtures to form CO and CO₂ [5, 6].

We have recently studied the combustion of a model soot over Na Al₂O₃ catalysts using both O₂ and NO/O₂ mixtures as oxidising agents [7]. The use of NO/O₂ as an oxidising agent promotes soot combustion over these materials – presumably through the operation of an NO₂ intermediate in the reaction mechanism (see scheme 1) [8]. We have also found that the presence of SO₄²⁻ remaining on the catalyst surface slightly promotes the combustion when O₂ is used as an oxidant. However, the improvements in activity noticed with NO/O₂ mixtures as an oxidant are not seen in the presence of SO₄²⁻.

In this work we extend this study to look at the effects that changing the [Na] on the Al₂O₃ supports as well as changing the support (from Al₂O₃ to SiO₂) have on this reaction system.
Furthermore, recent reports [9, 10] have suggested that the presence of a NO\textsubscript{x} trapping component within a catalyst formulation promotes particulate combustion in the presence of NO/O\textsubscript{2}. We also analyse the particulate combustion activity of a series of materials that have been prepared in particular for operation within a NO\textsubscript{x} trapping and reduction cycle, \textit{i.e.} Fe Ba ZSM-5 materials. Specifically in carrying out the latter experiments we analyse both the effect of the presence of the NO\textsubscript{x} trapping component on combustion activity as well as the influence of the partial pressure of NO\textsubscript{(g)} on combustion activity and selectivity to CO/CO\textsubscript{2}.

The final feature is of interest since it might help to clarify the intermediate role of the NO\textsubscript{2} $\rightarrow$ NO reduction within the reaction mechanism. One possible mode of action of NO\textsubscript{2} is for it to react with C\textsubscript{(s)} to form CO (which later oxidises to CO\textsubscript{2}) while the second is that it reacts with C\textsubscript{(s)} to form some activated surface intermediate (akin to a carbonyl) [11] which can then go on to react with either another NO\textsubscript{2} molecule or an O\textsubscript{2} to form CO\textsubscript{2}.

**Experimental.**

*Catalyst Preparation:*

1% and 10% Na Al\textsubscript{2}O\textsubscript{3} (and 1% Na SiO\textsubscript{2}) catalysts were prepared using conventional incipient wetness impregnation of either commercial $\gamma$-Al\textsubscript{2}O\textsubscript{3} (crushed and sieved between particle sizes of 212 and 600 $\mu$m) or commercial SiO\textsubscript{2} (washed in HNO\textsubscript{3} and calcined at 500 °C for 2 h) using solutions of NaNO\textsubscript{3}. “Blank” support samples were prepared by impregnation with NH\textsubscript{4}NO\textsubscript{3} followed by calcination. Sulphate was dosed onto the support either alone (by impregnating with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}) or with Na (by impregnating with Na\textsubscript{2}SO\textsubscript{4}). The samples were dried in an oven at 110 °C and calcined at
500 °C for 2 h. Previous experiments over Al₂O₃ supported catalysts [12] have shown that SO₄²⁻ remains on the catalyst surface following the calcination of SO₄²⁻ salts while NH₄⁺ cations and NO₃⁻ anions are removed (as NO₂) during calcination.

Fe ZSM and Ba ZSM were prepared by conventional ion-exchange method using Na ZSM-5 (SiO₂/Al₂O₃ = 27) obtained from Alsi-Penta. A quantity of 1.0 g zeolite was shaken for 2 h in 100 ml of either 0.01M FeSO₄.7H₂O or 0.01M Ba(C₂H₃O₂)₂. The samples were filtered, washed in hot de-ionised water, dried at 110 °C and calcined at 500 °C for 2 h. A composite catalyst containing both Fe and Ba (Fe Ba ZSM-5) was prepared using the pre-prepared Fe ZSM-5 and introducing the barium by a similar ion-exchange process. The elemental composition of each sample, as determined by acid digestion followed by atomic absorption spectroscopy, is given in Table 1. All samples were pressed and sieved to particle sizes of 212-600 µm prior to use.

*Activity measurements*

The ex-NO₃⁻ and ex-SO₄²⁻ Na Al₂O₃ and Na SiO₂ catalysts were physically mixed with samples of a model soot (Degussa Printex L in a ratio of 1 part catalyst:2 parts soot). The mixture was then compressed at a pressure of 5 tonnes in a Grazeby Specac press. The resultant pellets were crushed and sieved to particle sizes of between 212 and 600 µm. The Al₂O₃-supported catalyst/soot mixture (50 mg) was held, using plugs of quartz wool, in a glass reactor tube while mixtures of air and N₂ (4.7% O₂ in a total flow of 114 ml min⁻¹) or air, N₂ and NO/He (3.9% O₂ and 1387 ppm NO with a total flow of 137 ml min⁻¹) were flowed over the samples.
Different conditions were used for the SiO$_2$-supported catalysts. The catalyst/soot mixture (10 mg) was held in the reactor tube and a reactant mixture of either air (25 ml/min) or a mixture of air and NO (2857 ppm NO in a total flow of 35 ml min$^{-1}$) was used. The gases were flowed over the samples at various temperatures and samples of the exit gas were periodically analysed using on-line GC-FID detection (Shimadzu GC-8A fitted with a methanator). Peaks relating to the production of CO and CO$_2$ were monitored and converted into μmol produced min$^{-1}$ for presentation. Gases were from BOC or BOC Special Gases and were used without further purification.

Typically four samples of the exit gas were analysed at each temperature and in all cases steady state production of CO and CO$_2$ were obtained after 15 min in a stream of either air or NO/air at a particular temperature and then the temperature was raised by either 50 °C or 100 °C (between 300 °C and 550 °C) and the measurements repeated. Each catalyst/soot mixture was subjected to exactly the same regime and the catalyst/soot mixture was replaced between experiments.

The conversions of soot to CO and CO$_2$ under these conditions after ~ 5 minutes on stream are clearly not steady state conversions since clearly the concentration of one of the reactants, i.e. the soot, is constantly changing. However, given that the amount of combustion taking place is relatively small (generally <2 μmol CO$_x$ min$^{-1}$ at T≤500 °C) and that the amount of soot present at the beginning of an experiment is relatively large (2775 and 555 μmol for Al$_2$O$_3$ and SiO$_2$ catalysts respectively) we can say that a pseudo steady state reaction rate is achieved at each temperature. Transient experiments with continuous monitoring of CO$_x$ formation over these and related catalysts have confirmed this [13].
Temperature programmed oxidation measurements.

The zeolite-supported catalysts were mixed with soot and pressed and sieved as before. Fifty mg of these mixtures were held in a quartz tubular reactor. Mixtures of O₂ and He (6% O₂ in a total flow of 100 ml min⁻¹) or O₂, He and NO/He (with 6% O₂ and [NO] varying between 0 and 2774 ppm in a total flow of 100 ml min⁻¹) were flowed over the samples and the temperature was ramped at a rate of 20 °C /min between 50 °C and 550 °C. The outlet of the reactor was connected to a mass spectrometer (Prolab), which continuously analysed signals due to NO, CO and CO₂. The data are then corrected for overlapping masses (i.e. the contribution of the CO₂ fragment at 28 to the CO signal was removed).

Temperature programmed desorption measurements.

The NOₓ-storage capabilities of the 1% Na Al₂O₃ supported catalysts have been presented previously [7] and those of the SiO₂ supported materials were probed in a similar manner here using temperature-programmed desorption of NO. The catalyst (50 mg) was dosed with a mixture of NO + O₂ (1250 ppm NO + 22% O₂) at 100 °C until saturated and subsequently cooled to 50 °C in a flow of He. The temperature was ramped from 50 °C to 700 °C at a rate of 20 °C/min while the NO signal was continuously monitored by mass spectroscopy.
Results and Discussion.

Table 1 shows the pseudo steady state activities of the Na Al₂O₃ catalysts as a function of temperature, Na precursor, Na loading and oxidant used in the reaction. The presence of SO₄²⁻ on the surface has no detrimental effect on the combustion with air over the 1% catalyst, indeed a slight promotion is noted. The activity of the catalysts in both cases (ex-NO₃⁻ and ex-SO₄²⁻) are far higher with the higher loading of Na but the presence of SO₄²⁻ does poison activity of the 10% Na catalyst considerably.

In the presence of NO the ex-NO₃⁻ catalysts are also more active that they were when Air alone was used as an oxidant (especially above 500 °C). Increased Na loading also results in greater amounts of combustion in both cases. Note the final data point for the 10% Na catalyst in this plot represents a situation where the carbon in the reactor has been totally combusted by the end of the experiment. Thus a “true” steady state activity would be considerably higher than reported here. One possible reason for this increased activity in the presence of a higher Na loading might be an increased contact between the soot and the NaO portion of the catalyst as the NaO forms NaNO₂ and NaNO₃ upon interaction with NO and O₂. These materials melt at relatively low temperature (~281 °C and 308 °C respectively [14]) and can thus flow within the reactor during the combustion reaction [10] increasing contact with soot particles.

While there is no promoting effect of NO over the 1% catalyst in the presence of SO₄²⁻ (if anything combustion activity is decreased in the presence of NO) there is a definite promoting effect at the 10% loading. However this catalyst is still significantly less active than the 10% Na loaded catalyst in the absence of surface sulphate. This is presumably due to the poisoning effect of the sulphate [7, 15] which prevents NO
adsorption and thus NO oxidation – a necessary intermediate step in the combustion reaction.

Table 2 shows the activity of two SiO$_2$ supported 1% Na catalysts in the soot / O$_2$ and soot / O$_2$/NO reactions prepared again from NaNO$_3$ and Na$_2$SO$_4$ precursors. These experiments were performed under different reaction conditions to those of the Al$_2$O$_3$ supported materials so direct comparisons of these activities with those reported above are not possible. However, a qualitative analysis shows that the amount of CO$_x$ produced from the reaction with over the SiO$_2$-supported was greater than that produced over the Al$_2$O$_3$ supported materials (since similar amounts of CO$_x$ are formed in both cases but there is five times more soot present in the reaction mixture when the Al$_2$O$_3$ supported materials are used).

In addition, within this series of experiments it is possible to analyse the effect of both NO$_{(g)}$ and SO$_4^{2-}$ upon the soot combustion reaction – the main thrust of the current work.

There would be several expected effects related to the changing of the support from Al$_2$O$_3$ to SiO$_2$. These effects are associated with the interactions between NO$_x$ and SO$_4^{2-}$ and the two oxide surfaces. Firstly NO$_x$ adsorbs strongly and in relatively high concentrations on Al$_2$O$_3$ and in very low concentrations on SiO$_2$ [12,15]. This must favour any reaction in which involves promotion by NO$_x$. Secondly, surface SO$_4^{2-}$ species are very stable on Al$_2$O$_3$ [16] while they are unknown on SiO$_2$ supports [17]. Both of these factors will impinge on the mechanism of both the NO$_x$ promotion and the SO$_4^{2-}$ poisoning seen for the Al$_2$O$_3$ supported catalysts.
Table 3 (in the second and fourth columns) shows that the combustion activity of the ex-SO$_4^{2-}$ and ex-NO$_3^-$ catalysts are similar to one another when air is used as an oxidant. The addition of NO to the reactant stream (in the third and fifth columns) promotes lower temperature (<500 °C) combustion activity while, in contrast to the situation above the conversion of soot into CO and CO$_2$ actually decreases at temperatures of 500 °C and 550 °C. This poisoning effect is also more severe over the SO$_4^{2-}$ containing catalyst. This suggests that the oxidation of NO to NO$_2$ does not take place over the SiO$_2$ catalyst and thus the promotion effect seen above is removed. One possible explanation for the decreased activity in the presence of NO is competition between it and O$_2$ for surface adsorption sites.

This result suggests that the Al$_2$O$_3$ supported materials are better able to adsorb NO (as we knew from TPD measurements – see below) and form NO$_2$ (which promotes soot combustion) than the analogous SiO$_2$ supported catalysts. Previous work has shown that Al$_2$O$_3$ is not an effective NO oxidation catalysts [18] while other authors suggest that it has sufficient activity to oxidise NO to NO$_2$ before trapping NO$_2$ in a BaO NO$_x$ trap [19]. This work shows that it must, under these conditions have a certain activity for NO oxidation and also that this activity is greater than SiO$_2$ supports.

Figure 3 shows the temperature programmed desorption of NO$_x$ from SiO$_2$ and Na SiO$_2$ catalysts prepared using both NO$_3^-$ and SO$_4^{2-}$ precursors. It can be seen that SiO$_2$ supports alone do not adsorb NO$_x$ while doping the catalyst with 1% Na forms sites that lead to the formation of nitrate type species (as determined from the temperature of decomposition) on the catalyst surface (~ 200 μmol g$^{-1}$ NO$_x$ was adsorbed). Similar Al$_2$O$_3$ supported materials adsorb far more NO$_x$ under these conditions (~ 500 μmol g$^{-1}$)
presumably through adsorption upon the Al$_2$O$_3$ surface as well as on Na$^+$ or NaO species [7]. Further doping of this catalyst with SO$_4^{2-}$ removes these adsorption sites. As mentioned SO$_4^{2-}$ species are not stable on an SiO$_2$ surface [17] and SO$_4^{2-}$ species do not decompose (as NO$_3^-$ species do) during calcination [12] thus it would be expected that SO$_4^{2-}$ would exist in small Na$_2$SO$_4$ crystallites on the surface. The Na species here is unavailable to adsorb NO$_x$ while NaO species on SiO$_2$ from the ex-NO$_3^-$ catalyst above are available (as seen in from the TPD).

These results show that the Na-containing species on the SiO$_2$ surface (in the absence of surface SO$_4^{2-}$) is available to adsorb a certain amount of NO$_x$ but the activity results show that this NO$_{ads}$ does not promote the combustion reaction over the same catalyst (figure 2). Again this suggests that the support is intimately involved in the NO oxidation mechanism (a necessary step in the promotion) and that the Al$_2$O$_3$ support is more able to carry out this reaction than SiO$_2$.

Recently [9, 10] it has been reported that the addition of NO$_x$ trapping species to soot combustion catalysts increases soot combustion activity. This would make mechanistic sense if such systems led to large concentrations of surface nitrites and nitrates which could either interact further with NO$_x$ traps or go on to oxidise soot. Also it should be recalled that the oxidation of NO to NO$_2$ is a necessary step in both the NO$_x$ trapping process [20] and in the proposed promotion of the soot combustion reaction seen above.

With this in mind we have looked at the soot combustion activity of several systems which have previously been studied as NO$_x$ traps [21], i.e. Fe ZSM-5, Ba ZSM-5
and Fe Ba ZSM-5. Figure 2 shows the Temperature Programmed Combustion activity of all three catalysts under an O₂ atmosphere and in the presence of both NO and O₂.

The upper plots show the formation of COₓ in the presence of NO (2774ppm) / Air with the lower ones referring to the same reaction in the absence of NO. In all cases the concentration of NO did not dramatically change during the course of the reaction, i.e. no NO(g) was consumed. There is a small desorption of NOₓ seen at ~ 120 °C in all cases as physisorbed NO on the soot / catalyst system is removed (results not shown). However higher temperature desorptions – which would be expected from previous TPD analyses of these catalysts [21] have not been seen. We can assume that the relatively small amounts of NO desorbing under these conditions do not affect the overall NO signal (the experiment is carried out in 2274 ppm NO) and thus remain unnoticed.

In any case the presence of NOₓ has no dramatic effect on the conversions seen. On close examination the minor effects of the presence of NO include a slight poisoning of the reaction over Fe ZSM-5, a slight promotion of the reaction over Fe Ba ZSM-5 and little or no effect of the presence of NO over the Ba ZSM-5.

Thus we can say that in this system the presence of a NOₓ trapping component within the catalyst does not dramatically improve the combustion of soot. However, these results do not contradict those discussed by Jacquot et al. who see such an improvement in their systems [10]. In their experiments they were looking at the NOₓ trapping and regeneration in combination with particulate, hydrocarbon and CO combustion (“four-way” catalyst technology). They noticed an increase in particulate combustion when NOₓ traps were added to the system. This can be rationalised not as being due to the presence of the NOₓ trap itself but rather to two effects of NOₓ trap regeneration, i.e. the increased
temperature caused by the exotherm generated during regeneration and the increased amount of NO$_2$ present in the system each time the NO$_x$ trap is regenerated. This NO$_2$ is then better able to combust soot in the mechanism discussed above and the subsequently generated NO is then reduced to N$_2$ by the excess hydrocarbons available during the rich pulse of the regeneration.

Finally in this study we examined the above system in an effort to understand the role of the NO$_2$ / soot interaction in promoting the combustion of soot. We know that there is no overall decrease in the NO$_x$ concentration during the reaction and thus we can conclude that NO and NO$_2$ redox couples simply shuttle an O atom to the soot surface where it adsorbs. Presumably upon reaction this would form a surface carbonyl-type species [11].

There are two possible reaction routes for this carbonyl to take.

1. This species could be activated toward oxidation and go on to react with O$_2$ (or a second molecule of NO$_2$) to form CO$_2$(g) or

2. The carbonyl could desorb from the surface and form a CO$_2$(g) molecule. This CO$_2$(g) could then further react over the catalyst (with O$_2$) to form CO$_2$.

We have studied the composite material in the soot combustion reaction in the presence of varying concentrations of NO. If the former mechanism of interaction between NO$_2$ and the soot were to predominate then there should be no effect on the CO / CO$_2$ product distribution following a change in [NO]. However, if the NO$_2$/C$_s$ reaction produced gaseous CO we would expect an increase in [CO] as [NO] is increased.

Figure 3 shows the effect of varying the concentration of NO on the production of both CO and CO$_2$ over the combined Fe Ba ZSM-5 catalyst. Figure 3a shows that there is
no direct correlation between the amount of NO added and the production of CO₂. CO₂ production decreases at lower levels and increases at higher levels of NO. The major product of the reaction is CO₂.

A more interesting comparison is seen in Figure 3b where the CO profiles from the same reactions are shown. These show that CO is a minor product in the product mixture (~ 7%) and that the production of CO has a clear relationship with the amount of NO in the reactant mixture. This becomes very apparent at temperatures above 350 °C and suggests that the interaction between NO₂ (formed from oxidation of NO) and the soot produces CO₉(g) as a product rather than a surface oxygenate intermediate.

**Conclusions.**

This study has shown that the promotional effects of NO on the combustion of soot depends on the support used (with Al₂O₃ allowing more promotion than SiO₂) and on the presence of surface SO₄²⁻ since the production of NO₂ (a necessary intermediate in this promotion) is not promoted over SiO₂ and is hampered by the presence of SO₄²⁻ over Al₂O₃-based materials. The combustion activity increases with Na loading especially in the presence of NO and this latter point is ascribed to the formation of molten NaNO₂ and NaNO₃ on the catalysts and subsequent improved contact between the soot and the catalytic material.

We have also shown that the presence of a NOₓ trapping component *per se* does not improve the combustion activity of oxidation catalysts in the presence of NO₉(g). However, such improvement could be easily envisaged directly following the
regeneration of the NO$_3$ trap due to (a) an increase in temperature due to the exotherm caused during regeneration and (b) an increase in local [NO$_2$].

Finally the results presented above suggest that CO$_{(g)}$ is the primary product following the interaction between NO$_2$ and the soot surface.

**Acknowledgements:** We would like to gratefully acknowledge the Irish Research Council for Science, Engineering and Technology for support of this work under grant number SC/02/227 and Ms Linda Maguire and Ms Rachel Doyle for assistance in the preparation of the catalysts and carrying out preliminary experiments.

**References**


Table 1: Showing preparation conditions and content of the ZSM-5 materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe content (wt %)</th>
<th>Ba content (wt %)</th>
<th>Preparation procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-ZSM-5</td>
<td>0.82</td>
<td>-</td>
<td>Exchanging Na-ZSM-5 with FeSO$_4$.7H$_2$O for 2 h at room temperature</td>
</tr>
<tr>
<td>Ba-ZSM-5</td>
<td>-</td>
<td>4.3</td>
<td>Exchanging Na-ZSM-5 with Ba(C$_2$H$_3$O$_2$)$_2$ for 2 h at room temperature</td>
</tr>
<tr>
<td>Fe/Ba-ZSM-5</td>
<td>0.88</td>
<td>1.7</td>
<td>Exchanging Fe-ZSM-5 with Ba(C$_2$H$_3$O$_2$)$_2$ for 2 h at room temperature</td>
</tr>
</tbody>
</table>
Scheme 1: Showing proposed mechanism of promotion of soot combustion by NO\(_{(g)}\)
Table 2: Pseudo Steady State Activities ($\mu$mol min$^{-1}$ production of CO$_3$) of 1% and 10% Na Al$_2$O$_3$ catalysts (ex-NO$_3^-$ or ex-SO$_4^{2-}$) from soot combustion using Air and Air/NO mixtures as oxidants as a function of temperature. Note the data point at 550 °C (with *) for the 10 % ex-NO$_3^-$ catalyst is limited by amount of soot remaining in the reactor.

<table>
<thead>
<tr>
<th>% Na</th>
<th>1</th>
<th>1</th>
<th>10</th>
<th>10</th>
<th>1</th>
<th>1</th>
<th>10</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Oxidant</td>
<td>Air</td>
<td>NO/Air</td>
<td>Air</td>
<td>NO/Air</td>
<td>Air</td>
<td>NO/Air</td>
<td>Air</td>
<td>NO/Air</td>
</tr>
<tr>
<td>T / °C</td>
<td>300</td>
<td>0.000</td>
<td>0.050</td>
<td>0.044</td>
<td>0.107</td>
<td>0.000</td>
<td>0.050</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.057</td>
<td>0.058</td>
<td>2.105</td>
<td>1.463</td>
<td>0.063</td>
<td>0.171</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>0.071</td>
<td>0.189</td>
<td>3.481</td>
<td>4.657</td>
<td>0.100</td>
<td>0.231</td>
<td>0.182</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.270</td>
<td>0.589</td>
<td>8.139</td>
<td>13.145</td>
<td>0.450</td>
<td>0.456</td>
<td>2.051</td>
</tr>
</tbody>
</table>
Table 3

<table>
<thead>
<tr>
<th>SO$_4^{2-}$ (s)</th>
<th>No</th>
<th>No</th>
<th>Yes</th>
<th>Yes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidant</td>
<td>Air</td>
<td>Air / NO</td>
<td>Air</td>
<td>Air / NO</td>
</tr>
<tr>
<td>T / °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.031</td>
<td>0.178</td>
<td>0.026</td>
<td>0.205</td>
</tr>
<tr>
<td>400</td>
<td>0.147</td>
<td>0.500</td>
<td>0.124</td>
<td>0.522</td>
</tr>
<tr>
<td>450</td>
<td>0.388</td>
<td>0.869</td>
<td>0.343</td>
<td>0.741</td>
</tr>
<tr>
<td>500</td>
<td>1.542</td>
<td>1.470</td>
<td>1.272</td>
<td>1.005</td>
</tr>
<tr>
<td>550</td>
<td>5.833</td>
<td>3.199</td>
<td>6.054</td>
<td>1.213</td>
</tr>
</tbody>
</table>

Table 3: Pseudo steady state activities ($\mu$mol min$^{-1}$ production of CO$_x$) from soot combustion over Na SiO$_2$ (ex SO$_4^{2-}$ and ex NO$_3^-$) catalysts using Air and Air/NO mixtures as oxidants.
Figure 1: Temperature Programmed Desorption of NO$_x$ from a series of SiO$_2$-supported catalysts, (◊) SiO$_2$, (○) Na SiO$_2$, (□) SO$_4^{2-}$ SiO$_2$, (◆) Na SO$_4^{2-}$ SiO$_2$. 
Figure 2: Temperature programmed combustion activity in the presence of Air (lower plots) and NO/Air (displaced upper plots). Fe ZSM-5(●), Ba ZSM-5(▲) and Fe Ba ZSM-5(8).
Figure 3: Temperature Programmed CO$_2$ (Figure 3a) and CO (Figure 3b) formation in the presence of varying amounts of [NO], 0 ppm (∅), 730 ppm (∇), 1387 ppm (Δ) and 2774 ppm (∇).