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Catalysis Today 114 (2006) 340–345

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The combustion of carbon particulates using NO/O_2 mixtures: The influence of SO_4^{2-} and NO_x trapping materials

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Abstract

The activity of several catalysts are studied in the soot combustion reaction using air and NO/air as oxidising agents. Over Al_2O_3-supported catalysts $NO_{(g)}$ is a promoter for the combustion reaction with the extent of promotion depending on the Na loading. Over these catalysts SO_4^{2-} poisons this promotion by preventing NO oxidation through a site blocking mechanism. SiO_2 is unable to adsorb NO or catalyse its oxidation and over SiO_2-supported Na catalysts $NO_{(g)}$ inhibits the combustion reaction. This is ascribed to a competition between NO and O_2. Over Fe-ZSM-5 catalysts the presence of a NO_x 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 NO_x trap operation as NO_2 is periodically released during regeneration and thus available for soot combustion. Experiments during which the $[NO]_{(g)}$ is varied show that CO, rather than an adsorbed carbonyl-like intermediate, is formed upon reaction between NO_2 (the proposed oxygen carrier) and soot.

Keywords: Particulates; SiO_2; Al_2O_3; SO_4^{2-}; Fe-ZSM-5; NO_x trap

1. 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 O_2 and/or NO/O_2 mixtures to form CO and CO_2 [5,6].

We have recently studied the combustion of a model soot over Na Al_2O_3 catalysts using both O_2 and NO/O_2 mixtures as oxidising agents [7]. The use of NO/O_2 as an oxidising agent promotes soot combustion over these materials, presumably through the operation of an NO_2 intermediate in the reaction mechanism (see Scheme 1) [8]. We have also found that the presence of SO_4^{2-} remaining on the catalyst surface slightly promotes the combustion when O_2 is used as an oxidant. However, the improvements in activity noticed with NO/O_2 mixtures as an oxidant are not seen in the presence of SO_4^{2-}.

In this work we extend this study to look at the effects that changing the [Na] on the Al_2O_3 supports as well as changing the support (from Al_2O_3 to SiO_2) have on this reaction system.

Furthermore, recent reports [9,10] have suggested that the presence of a NO_x trapping component within a catalyst formulation promotes particulate combustion in the presence of NO/O_2. We also analyse the particulate combustion activity of a series of materials that have been prepared in particular for operation within a NO_x trapping and reduction cycle, 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_x trapping component on combustion activity as well as the influence of the partial pressure of $NO_{(g)}$ on combustion activity and selectivity to CO/CO_2.

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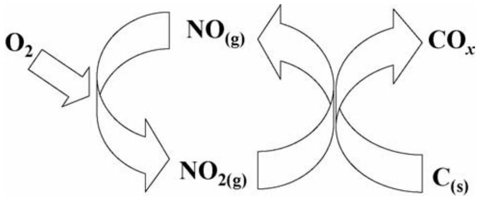
doi:10.1016/j.cattod.2006.02.036



Scheme 1. Showing proposed mechanism of promotion of soot combustion by $NO_{(g)}$.

The final feature is of interest since it might help to clarify the intermediate role of the $NO_2 \rightarrow NO$ reduction within the reaction mechanism. One possible mode of action of NO_2 is for it to react with $C_{(s)}$ to form CO (which later oxidises to CO_2) while the second is that it reacts with $C_{(s)}$ to form some activated surface intermediate (akin to a carbonyl) [11] which can then go on to react with either another NO_2 molecule or an O_2 to form CO_2.

2. Experimental

2.1. Catalyst preparation

One percent and 10% Na Al_2O_3 (and 1% Na SiO_2) catalysts were prepared using conventional incipient wetness impregnation of either commercial γ-Al_2O_3 (crushed and sieved between particle sizes of 212 and 600 μm) or commercial SiO_2 (washed in HNO_3 and calcined at 500 °C for 2 h) using solutions of $NaNO_3$. ‘‘Blank’’ support samples were prepared by impregnation with NH_4NO_3 followed by calcination. Sulphate was dosed onto the support either alone (by impregnating with $(NH_4)_2SO_4$) or with Na (by impregnating with Na_2SO_4). The samples were dried in an oven at 110 °C and calcined at 500 °C for 2 h. Previous experiments over Al_2O_3-supported catalysts [12] have shown that SO_4^{2-} remains on the catalyst surface following the calcination of SO_4^{2-} salts while NH_4^+ cations and NO_3^- anions are removed (as NO_2) during calcination.

Fe-ZSM and Ba-ZSM were prepared by conventional ion-exchange method using Na-ZSM-5 ($SiO_2/Al_2O_3 = 27$) obtained from Alsi-Penta. A quantity of 1.0 g zeolite was shaken for 2 h in 100 ml of either 0.01 M $FeSO_4 \cdot 7H_2O$ or 0.01 M $Ba(C_2H_3O_2)_2$. The samples were filtered, washed in hot deionised 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.

2.2. Activity measurements

The ex-NO_3^- and ex-SO_4^{2-} Na Al_2O_3 and Na SiO_2 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 Al_2O_3-supported catalyst/soot mixture (50 mg) was held, using plugs of quartz wool, in a glass reactor tube while mixtures of air and N_2 (4.7% O_2 in a total flow of 114 ml min^{-1}) or air, N_2 and NO/He (3.9% O_2 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^{-1}) 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 per min 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 or 100 °C (between 300 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 min on stream are 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 $T \leq 500$ °C) and that the amount of soot present at the beginning of an experiment is relatively large (2775 and 555 μmol for Al_2O_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].

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

Sample	Fe content (wt %)	Ba content (wt %)	Preparation procedure
Fe-ZSM-5	0.82	–	Exchanging Na-ZSM-5 with $FeSO_4 \cdot 7H_2O$ for 2 h at room temperature
Ba-ZSM-5	–	4.3	Exchanging Na-ZSM-5 with $Ba(C_2H_3O_2)_2$ for 2 h at room temperature
Fe/Ba-ZSM-5	0.88	1.7	Exchanging Fe-ZSM-5 with $Ba(C_2H3O_2)_2$ for 2 h at room temperature

2.3. Temperature programmed oxidation measurements

The zeolite-supported catalysts were mixed with soot and pressed and sieved as before. Fifty milligrams of these mixtures were held in a quartz tubular reactor. Mixtures of O_2 and He (6% O_2 in a total flow of 100 ml min^{-1}) or O_2, He and NO/He (with 6% O_2 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^{-1} between 50 and 550 °C. The outlet of the reactor was connected to a mass spectrometer (Prolab), which continuously analysed signals due to NO, CO and CO_2. The data are then corrected for overlapping masses (i.e. the contribution of the CO_2 fragment at 28 to the CO signal was removed).

2.4. Temperature programmed desorption measurements

The NO_x-storage capabilities of the 1% Na Al_2O_3-supported catalysts have been presented previously [7] and those of the SiO_2-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 + O_2 (1250 ppm NO + 22% O_2) at 100 °C until saturated and subsequently cooled to 50 °C in a flow of He. The temperature was ramped from 50 to 700 °C at a rate of 20 °C min^{-1} while the NO signal was continuously monitored by mass spectroscopy (Fig. 1).

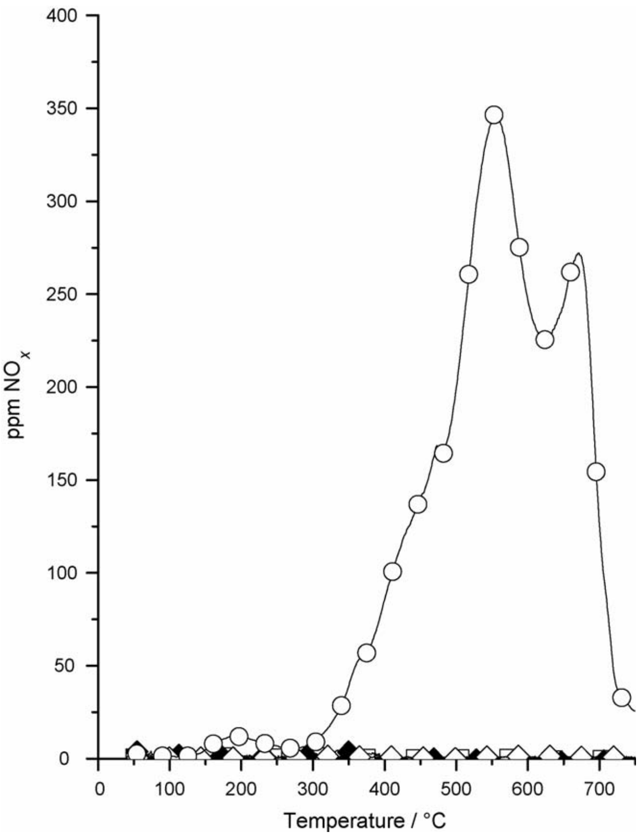


Fig. 1. Temperature programmed desorption of NO_x from a series of SiO_2-supported catalysts, (◇) SiO_2, (○) Na SiO_2, (□) SO_4^{2-} SiO_2, (◆) Na SO_4^{2-} SiO_2.

3. Results and discussion

Table 2 shows the pseudo steady state activities of the Na Al_2O_3 catalysts as a function of temperature, Na precursor, Na loading and oxidant used in the reaction. The presence of SO_4^{2-} 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-NO_3^- and ex-SO_4^{2-}) are far higher with the higher loading of Na but the presence of SO_4^{2-} does poison activity of the 10% Na catalyst considerably.

In the presence of NO the ex-NO_3^- 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 $NaNO_2$ and $NaNO_3$ upon interaction with NO and O_2. These materials melt at relatively low temperature (~281 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 SO_4^{2-} (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 3 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_2SO_4 precursors. These experiments were performed under different reaction conditions to those of the Al_2O_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_2O_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_2O_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_2O_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_2O_3 and in very low concentrations on SiO_2 [12,15]. This must favour any reaction which involves promotion by NO_x. Secondly, surface SO_4^{2-}

Table 2
Pseudo steady state activities (μmol min^{-1} production of CO_x) of 1% and 10% Na Al_2O_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

Na (%)	1	1	10	10	1	1	10	10
$SO_4^{2-}{}_{(s)}$	No	No	No	No	Yes	Yes	Yes	Yes
Oxidant	Air	NO/air	Air	NO/air	Air	NO/air	Air	NO/air
T (°C)								
300	0.000	0.050	0.044	0.107	0.000	0.050	0.035	0.137
400	0.057	0.058	2.105	1.463	0.063	0.171	0.123	0.203
450	0.071	0.189	3.481	4.657	0.100	0.231	0.182	0.387
500	0.270	0.589	8.139	13.145	0.450	0.456	2.051	1.744
550	1.086	1.606	9.410	9.601*	1.350	1.104	3.623	6.791

Note the data point at 550 °C (with asterisk (*)) for the 10% ex-NO_3^- catalyst is limited by amount of soot remaining in the reactor.

species are very stable on Al_2O_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_2O_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 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_2O_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_2O_3 is not an effective NO oxidation catalyst [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.

Fig. 1 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_2O_3-supported materials adsorb far more NO_x under these conditions (~500 μmol g^{-1}) presumably through adsorption upon the Al_2O_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_2SO_4 crystallites on the surface. The Na species here is unavailable to adsorb

Table 3
Pseudo steady state activities (μmol 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

$SO_4^{2-}{}_{(s)}$	No	No	Yes	Yes
Oxidant	Air	Air/NO	Air	Air/NO
T (°C)				
300	0.031	0.178	0.026	0.205
400	0.147	0.500	0.124	0.522
450	0.388	0.869	0.343	0.741
500	1.542	1.470	1.272	1.005
550	5.833	3.199	6.054	1.213

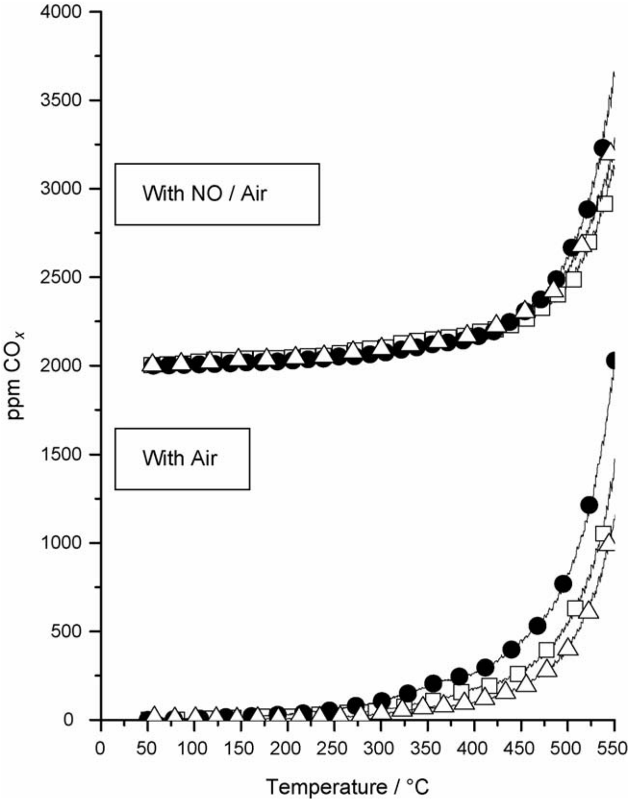


Fig. 2. Temperature programmed combustion activity in the presence of air (lower plots) and NO/air (displaced upper plots). Fe-ZSM-5 (●), Ba-ZSM-5 (□) and Fe/Ba-ZSM-5 (Δ).

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 $NO_{x\mathrm{ads}}$ does not promote the combustion reaction over the same catalyst (Table 3). Again this suggests that the support is intimately involved in the NO oxidation mechanism (a necessary step in the promotion) and that the Al_2O_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. Fig. 2 shows the temperature programmed combustion activity of all three catalysts under an O_2 atmosphere and in the presence of both NO and O_2.

The upper plots show the formation of CO_x in the presence of NO (2774 ppm)/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 NO_x seen at $\sim$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 NO_x 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 NO_x 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 NO_x trapping and reduction in combination with particulate, hydrocarbon and CO combustion (''four-way'' catalyst technology). They noticed an increase in particulate combustion when NO_x traps were added to the system. This can be rationalised not as being due to the presence of the NO_x trap itself but rather to two effects of NO_x 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

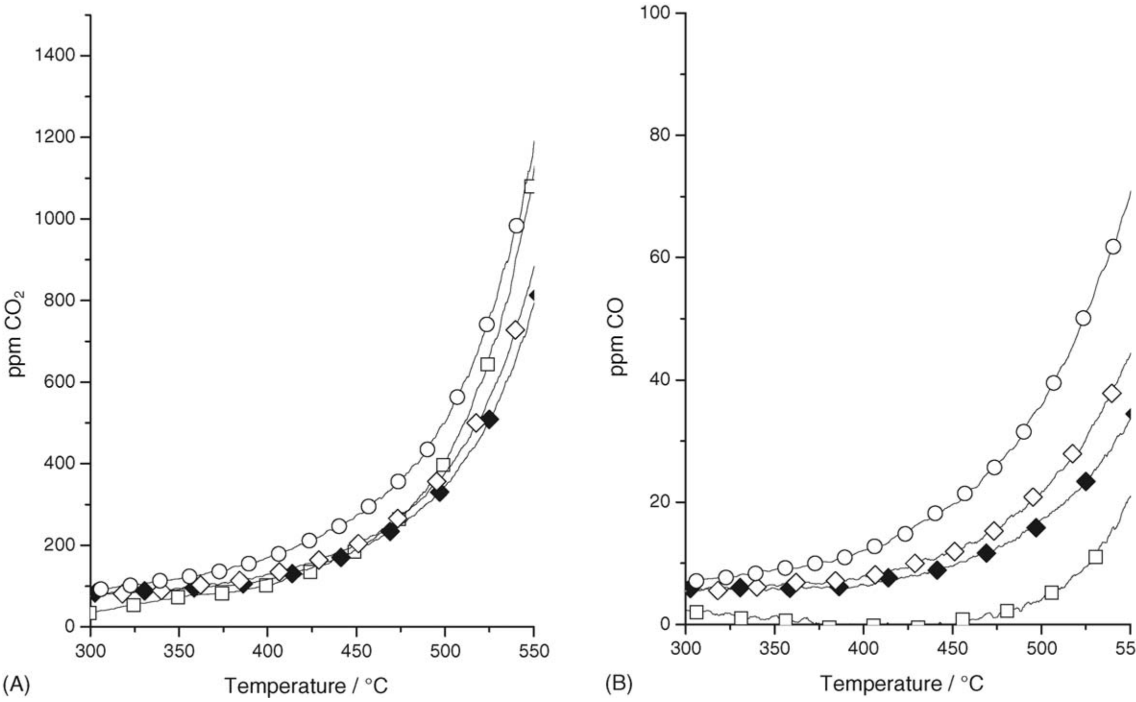


Fig. 3. Temperature programmed CO_2 (A) and CO (B) formation in the presence of varying amounts of [NO], 0 ppm (□), 730 ppm (◆), 1387 ppm (◇) and 2774 ppm (○).

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 $CO_{2(g)}$.
2. The carbonyl could desorb from the surface and form a $CO_{(g)}$ molecule. This $CO_{(g)}$ 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.

Fig. 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. Fig. 3A shows that there is no direct correlation between the amount of NO added and the production of CO_2. CO_2 production decreases at lower levels and increases at higher levels of NO. The major product of the reaction is CO_2.

A more interesting comparison is seen in Fig. 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 NO_2 (formed from oxidation of NO) and the soot produces $CO_{(g)}$ as a product rather than a surface oxygenate intermediate.

4. Conclusions

This study has shown that the promotional effects of NO on the combustion of soot depends on the support used (with Al_2O_3 allowing more promotion than SiO_2) and on the presence of surface SO_4^{2-} since the production of NO_2 (a necessary intermediate in this promotion) is not promoted over SiO_2 and is hampered by the presence of SO_4^{2-} over Al_2O_3-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 $NaNO_2$ and $NaNO_3$ on the catalysts and subsequent improved contact between the soot and the catalytic material.

We have also shown that the presence of a NO_x trapping component per se does not improve the combustion activity of oxidation catalysts in the presence of $NO_{(g)}$. However, such improvement could be easily envisaged directly following the regeneration of the NO_x 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.

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