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The influence of SO$_4^{2-}$ on the catalytic combustion of soot using O$_2$ and NO/O$_2$ mixtures over Na-promoted Al$_2$O$_3$ catalysts.

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Abstract.

Na/Al$_2$O$_3$ catalysts are tested in the soot oxidation reaction using O$_2$ and NO/O$_2$ as oxidising agents. The activity of the catalysts varies with oxidising agent and the presence of surface SO$_4^{2-}$.

NO$_{(g)}$ increases conversion of soot to CO$_x$. Surface SO$_4^{2-}$ has no effect on activity for the C$_{\text{(s)}}$+O$_2$ reaction but shows decreased activity in the Carbon+NO/O$_2$ oxidation. This is interpreted in terms of SO$_4^{2-}$ blocking NO adsorption sites, thus poisoning the NO+O$_2$ $\rightarrow$ NO$_2$ reaction, which is essential for the NO$_x$ promoted oxidation.

Keywords: Soot Combustion, Sulphate, NO$_x$.

1. Introduction

One of the major pollutants formed during the combustion of fossil fuels are carbonaceous particles\(^1\). These particles range in size between $<10$ $\mu$m in diameter up to visible soot and have several detrimental consequences for the environment. These range from (in the case of larger particles) the defacing of urban buildings and contributing significantly to global warming (particulates which land on arctic ice decrease the albedo of the ice leading to increased UV absorbance and subsequent increased rates of melting of ice)\(^2\) to, in the case of smaller particles, serious human
health implications as these can penetrate and lodge within the alveoli of the lung. It is thought that the particles are primarily carbonaceous in nature although it is reported also that they form using sulphate species as nucleation sites.

One proposed technique for the destruction of these species involves their trapping and subsequent oxidation to CO$_2$ using O$_2$ or NO/O$_2$ mixtures. In the latter case the NO is thought to act as an O-atom carrier between O$_2$ and the carbonaceous species through the formation and reduction of NO$_2$. NO$_2$ is a more oxidising material than O$_2$ and the presence of NO increases the conversion of soot to CO and CO$_2$.

If this cycle were to take place on the surface of a catalyst rather than both at the surface and in the gas phase then it could be envisaged as being similar to a nitrite/nitrate-type redox cycle (where nitrite corresponds to adsorbed NO and nitrate to adsorbed NO$_2$). Alkali metals form stable nitrite and nitrate type species on Al$_2$O$_3$ and for this reason they have been studied as possible catalysts for the combustion of carbonaceous particles.

Generally SO$_4$$^{2-}$ has been regarded as a poison for catalysts and catalytic processes although recently it has been found to promote such reactions as propane combustion and NO$_x$ reduction using NH$_3$ as a reducing agent. Previous work has shown that SO$_4$$^{2-}$ remains anchored to an Al$_2$O$_3$ surface when sulphate salts are used as catalyst precursors while related work has demonstrated that SO$_4$$^{2-}_{\text{ads}}$ blocks adsorption sites for NO and NO$_2$. With respect to sulphation Ciambelli et al. have noted that combustion activity (of a V/Cu/C/Ti-containing) alumino-silicate filter) decreases drastically once the filter is pre-sulphated but that this decrease is ameliorated somewhat by the addition of NO to the gas phase. In this work we analyse the effects of SO$_4$$^{2-}$ on the activity of Al$_2$O$_3$-supported catalysts for soot combustion.
2. Experimental

2.1. Sample Preparation.

1% Na/Al₂O₃ catalysts were prepared using conventional incipient wetness impregnation of commercial γ-Al₂O₃ (crushed and sieved between particle sizes of 212-600 µm) using solutions of NaNO₃. Sulphate was dosed on to the support either alone (by impregnating with (NH₄)₂SO₄) or with Na (by impregnating with Na₂SO₄). “Blank” support samples were prepared by impregnation with NH₄NO₃. The samples were dried in an oven at 110 °C and calcined at 500 °C for 2 h. Previous experiments over Al₂O₃ supported catalysts 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 calcination¹⁰.

2.2. Activity Measurements.

The 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 212-600 µm. 50 mg of these mixtures were held, using plugs of quartz wool, in a glass reactor tube. 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 at various temperatures and samples of the exit gas were periodically removed and analysed using on-line GC-FID detection (Shimadzu fitted with a methanator). Peaks relating to CO and CO₂ were monitored and converted into µmol for presentation. Gases were from BOC or BOC Special Gases and were used without further purification.
Typically steady state production of CO and CO₂ were obtained after ~ 15 minutes in a stream of either O₂ or NO/O₂ 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.

**Temperature Programmed Desorption Measurements**

A quartz tubular reactor was loaded with 50 mg of the samples of interest and dosed with a mixture of NO + O₂ (1250 ppm NO + 22% O₂) at 100 °C until saturated. The outlet of the reactor was connected to a mass spectrometer (Prolab), which continuously analysed signals due to NO and O₂. Once the catalyst was saturated the NOₓ and O₂ were then removed from the gas phase and the sample cooled to 50 °C in a flow of He. The Temperature was then ramped at a rate of 20 °C / min between 50 and 650 °C while the NO signal was continuously monitored.

3. **Results and discussion**

3.1 Activity Measurements.

Figure 1 compares the combustion activities of two 1% Na/Al₂O₃ catalysts (made from NO₃⁻ and SO₄²⁻ precursors) for the production of COₓ using O₂ and NO/O₂ mixtures respectively as oxidants. The ex-SO₄²⁻ catalyst is as active (indeed slightly more active) than the ex-NO₃⁻ material when air is used as an oxidant so it is clear that the presence of SO₄²⁻ in no way hinders the reaction that takes place between the O₂ and Cₙ(s). Activity is related to temperature and also to Na loading with a 5% and 10 % Na catalysts being substantially more active than the 1% (results not shown).
Figure 2 shows the activity of the same catalysts when soot is oxidised using mixtures of NO and O\textsubscript{2}. Over the ex-NO\textsubscript{3}\textsuperscript{-} catalyst these activities are higher than in the case were O\textsubscript{2} was the oxidant. It is known that this increased activity is due to the formation of NO\textsubscript{2}(g), which subsequently reacts with the soot to form CO (or CO\textsubscript{2} or CO\textsubscript{ads}) and regenerate NO\textsuperscript{3}. There is no reduction of NO\textsubscript{2} (as measured using a chemiluminescent NO\textsubscript{x} analyser) to any species other than NO (total NO\textsubscript{x} remains constant throughout the reaction).

The promoting effect seen in the case of the ex-NO\textsubscript{3}\textsuperscript{-} catalysts is not seen over the ex-SO\textsubscript{4}\textsuperscript{2-} materials. The conversion of soot to CO\textsubscript{x} is decreased in the presence of NO at all the temperatures studied. Thus it seems that the presence of SO\textsubscript{4}\textsuperscript{2-} on the surface has no effect on the Na/Al\textsubscript{2}O\textsubscript{3} activity for the C + O\textsubscript{2} reaction, but the improved activity of the catalyst seen in the presence of NO is not seen when SO\textsubscript{4}\textsuperscript{2-} is present. Temperature programmed desorption of NO\textsubscript{x} was used as a probe to attempt to explain these observations in terms of the proposed NO/NO\textsubscript{2} redox cycle.

3.2 Temperature Programmed Desorption Measurements.

Figure 3 shows Temperature Programmed Desorption profiles relating to the Desorption of NO\textsubscript{x} from Al\textsubscript{2}O\textsubscript{3}, 1% Na/Al\textsubscript{2}O\textsubscript{3}, 1% Na/Al\textsubscript{2}O\textsubscript{3} (ex SO\textsubscript{4}\textsuperscript{2-}) and Al\textsubscript{2}O\textsubscript{3} (treated with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and calcined). As has been previously seen in TPDs of NO\textsubscript{x} from Al\textsubscript{2}O\textsubscript{3}-based catalysts there are two areas of desorption, i.e. 150-250 °C and 450 – 600 °C. The latter peak is accompanied by desorption of O\textsubscript{2} and relates to the decomposition of surface nitrates and the former peak relates to the decomposition of surface nitrites\textsuperscript{11}.

Previous results showing the effect of sulphation\textsuperscript{11} (via SO\textsubscript{2} adsorption and oxidation) on the NO\textsubscript{x} adsorption capacity of Al\textsubscript{2}O\textsubscript{3}-based catalysts have shown that
the concentration of nitrate-type surface sites decreased following sulphation. This has been explained in terms of SO$_4^{2-}$ species irreversibly adsorbing on these site. Similar results are seen here for these 1%Na-containing catalysts.

The effect of doping the catalysts with 1%Na can be analysed by comparing the profiles relating to the Na/Al$_2$O$_3$ and Al$_2$O$_3$ catalysts. There are slightly higher concentrations of surface sites available for the formation of both nitrite and nitrate species in the presence of Na. The stability of the nitrite type species (as measured by the temperature of maximum desorption) is unchanged by the presence of Na while the nitrate type species are more stable in the presence of Na (compare a temperature of maximum desorption of 520 °C in the presence of Na and 496 °C in the absence of Na).

The presence of surface SO$_4^{2-}$ removes (presumably through the surface poisoning mechanism discussed above) almost all of the adsorption sites that lead to the formation of surface nitrates. Sulphate increases the concentration of sites available for nitrite formation (see table 1). This is possibly due to a conversion of some of the sites that were available for nitrate formation into those suitable for nitrite formation through the blocking of a surface oxygen site. However this is a relatively small effect and in the presence of both Na and SO$_4^{2-}$ it is not noticeable.

These sulphated catalysts are as active as the un-sulphated materials in the soot oxidation with O$_2$ but are less active than the un-sulphated analogues when the NO promoter is included in the reaction stream. It is certain that the presence of SO$_4^{2-}$ decreases the positive effect of NO$_x$ on the reaction and TPD studies show that this decrease is probably related to the blocking of the NO oxidation pathway, which is intimately involved in the NO$_x$ promotion mechanism.
It seems that in the absence of SO$_4^{2-}$ the Al$_2$O$_3$ surface is a sufficiently good catalyst to oxidise NO to NO$_2$ (as has been reported over BaO/Al$_2$O$_3$ NO$_x$ trapping materials$^{15}$ where the oxidation of NO to O$_2$ is also a required first step in the formation of Ba(NO$_3$)$_2$) but in the presence of SO$_4^{2-}$ this activity is lost since adsorption sites required for the first step in the oxidation are lost.

4. Conclusions

The activity of 1%Na/Al$_2$O$_3$ catalysts for the combustion of soot is related to the presence of NO as a gas phase promoter and the presence of SO$_4^{2-}$ remaining on the catalyst surface.

NO in the gas phase increases the activity of Na/Al$_2$O$_3$ catalysts for the soot combustion reaction. This promotional effect is considered to operate through the formation and utilisation of NO$_2$ and is lost when SO$_4^{2-}$ is present with Na on the Al$_2$O$_3$ surface. Surface SO$_4^{2-}$ also decreases the concentration of NO adsorption sites. These sites are important in the overall mechanism of NO promotion of the combustion reaction since NO adsorbs onto the catalyst before it is oxidised to NO$_2$. NO$_{(g)}$ forms adsorbed nitrites which are subsequently oxidised to adsorbed nitrates. The latter desorb as NO$_2$ and go on to oxidise the soot. Thus a decrease in the concentration of NO$_{ads}$ sites directly changes the activity of the system for the production of CO and CO$_2$.

This disruptive effect of oxidised sulphur species on the NO$_x$ oxidation reaction (and thus on overall soot combustion) should be taken into account when studying the activity of various catalysts in model soot oxidation studies since SO$_2$ is generally present in exhaust gases (leading to catalyst adsorbed sulphate under
oxidising conditions) and also when it is considered that the particulates themselves are considered to form around sulphate cores.

Acknowledgements

We would like to gratefully acknowledge the Irish Research Council for Science, Engineering and Technology for partly funding this work under grant number SC/02/227. The Faculty of Science UCD is also gratefully acknowledged for the provision of a start-up grant.

References


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Table 1 showing the amounts and maximum temperature of NO desorbed in each NO$_x$-TPD experiment.
Figures

Figure 1, Histogram showing μmol CO_x formed min^{-1} over 1% Na/Al_2O_3 catalyst (white) and a 1% Na/Al_2O_3 catalyst containing SO_4^{2-} (black) using O_2 as an oxidising agent.

Figure 2, Histogram showing μmol CO_x formed min^{-1} over 1% Na/Al_2O_3 catalyst (white) and a 1% Na/Al_2O_3 catalyst containing SO_4^{2-} (black) using mixtures of NO and O_2 as an oxidising agent.
Figure 3. Temperature Programmed Desorption of NO$_x$ from various Al$_2$O$_3$-supported catalysts. (■) Al$_2$O$_3$, (●) Na/Al$_2$O$_3$, (▲) Al$_2$O$_3$/S, (△) Na/Al$_2$O$_3$/S.