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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_2O_3 catalysts.

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Abstract.

Na/ Al_2O_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-} .

$\text{NO}_{(\text{g})}$ increases conversion of soot to CO_x . Surface SO_4^{2-} has no effect on activity for the $\text{C}_{(\text{s})}+\text{O}_2$ 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 $\text{NO}+\text{O}_2 \rightarrow \text{NO}_2$ 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 particles¹. These particles range in size between $< 10 \mu\text{m}$ 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 lung³. It is thought that the particles are primarily carbonaceous in nature although it is reported also that they form using sulphate species as nucleation sites⁴.

One proposed technique for the destruction of these species involves their trapping and subsequent oxidation to CO₂ using O₂ or NO/O₂ mixtures⁵. In the latter case the NO is thought to act as an O-atom carrier between O₂ and the carbonaceous species through the formation and reduction of NO₂. NO₂ is a more oxidising material than O₂ and the presence of NO increases the conversion of soot to CO and CO₂.

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 NO₂). Alkali metals form stable nitrite and nitrate type species on Al₂O₃ and for this reason they have been studied as possible catalysts for the combustion of carbonaceous particles⁶.

Generally SO₄²⁻ has been regarded as a poison for catalysts and catalytic processes⁷ although recently it has been found to promote such reactions as propane combustion⁸ and NO_x reduction using NH₃ as a reducing agent⁹. Previous work¹⁰ has shown that SO₄²⁻ remains anchored to an Al₂O₃ surface when sulphate salts are used as catalyst precursors while related work has demonstrated that SO₄²⁻_{ads} blocks adsorption sites for NO and NO₂¹¹⁻¹³. With respect to sulphation Ciambelli¹⁴ *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 SO₄²⁻ on the activity of Al₂O₃-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 μ m) 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 μ m. 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 114ml 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 μ mol 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 NO_x 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 CO_x 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 C_(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 O₂. Over the ex-NO₃⁻ catalyst these activities are higher than in the case where O₂ was the oxidant. It is known that this increased activity is due to the formation of NO_{2(g)}, which subsequently reacts with the soot to form CO (or CO₂ or CO_{ads}) and regenerate NO⁵. There is no reduction of NO₂ (as measured using a chemiluminescent NO_x analyser) to any species other than NO (total NO_x remains constant throughout the reaction).

The promoting effect seen in the case of the ex-NO₃⁻ catalysts is not seen over the ex-SO₄²⁻ materials. The conversion of soot to CO_x is *decreased* in the presence of NO at all the temperatures studied. Thus it seems that the presence of SO₄²⁻ on the surface has no effect on the Na/Al₂O₃ activity for the C + O₂ reaction, but the improved activity of the catalyst seen in the presence of NO is not seen when SO₄²⁻ is present. Temperature programmed desorption of NO_x was used as a probe to attempt to explain these observations in terms of the proposed NO / NO₂ redox cycle.

3.2 Temperature Programmed Desorption Measurements.

Figure 3 shows Temperature Programmed Desorption profiles relating to the Desorption of NO_x from Al₂O₃, 1% Na/Al₂O₃, 1% Na/Al₂O₃ (ex SO₄²⁻) and Al₂O₃ (treated with (NH₄)₂SO₄ and calcined). As has been previously seen in TPDs of NO_x from Al₂O₃-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 O₂ and relates to the decomposition of surface nitrates and the former peak relates to the decomposition of surface nitrites¹¹.

Previous results showing the effect of sulphation¹¹ (via SO₂ adsorption and oxidation) on the NO_x adsorption capacity of Al₂O₃-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_2O_3 and Al_2O_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_2O_3 surface is a sufficiently good catalyst to oxidise NO to NO_2 (as has been reported over $\text{BaO}/\text{Al}_2\text{O}_3$ NO_x trapping materials¹⁵ where the oxidation of NO to O_2 is also a required first step in the formation of $\text{Ba}(\text{NO}_3)_2$) 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_2O_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_2O_3 catalysts for the soot combustion reaction. This promotional effect is considered to operate through the formation and utilisation of NO_2^5 and is lost when SO_4^{2-} is present with Na on the Al_2O_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 . $\text{NO}_{(\text{g})}$ 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.

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	T _{max} Nitrite	NO desorbed μmol g ⁻¹	T _{max} Nitrate	NO desorbed μmol g ⁻¹
Al ₂ O ₃	164	13	496	286
Na/Al ₂ O ₃	193	48	530	304
Al ₂ O ₃ / SO ₄ ²⁻	234	38	496	9
Na/Al ₂ O ₃ /SO ₄ ²⁻	185	51	510	5

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

Figures

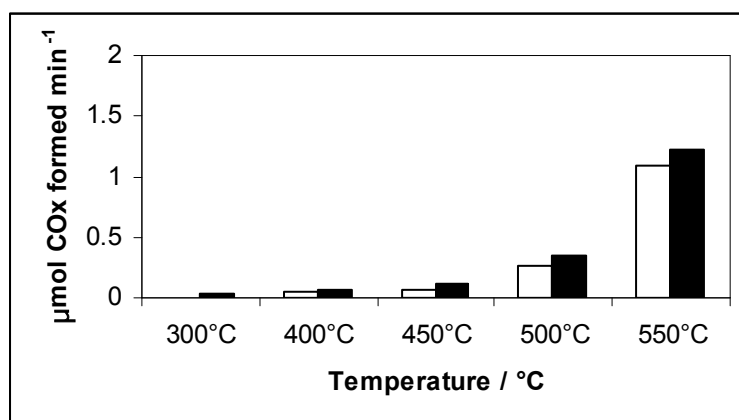


Figure 1, Histogram showing $\mu\text{mol CO}_x \text{ formed min}^{-1}$ over 1% Na/Al₂O₃ catalyst (white) and a 1% Na/Al₂O₃ catalyst containing SO₄²⁻ (black) using O₂ as an oxidising agent.

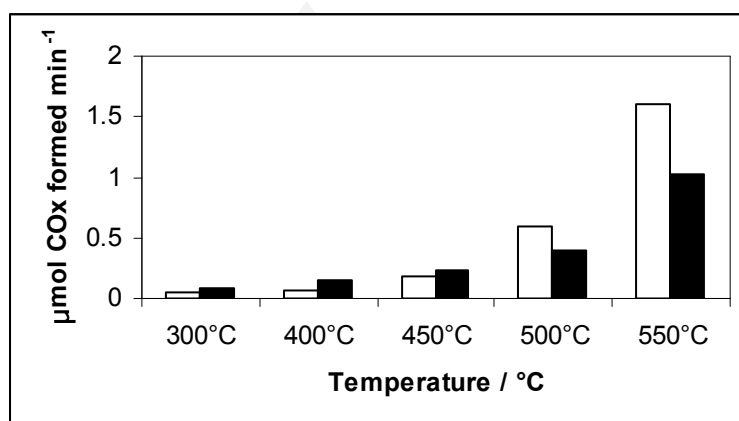


Figure 2, Histogram showing $\mu\text{mol CO}_x \text{ formed min}^{-1}$ over 1% Na/Al₂O₃ catalyst (white) and a 1% Na/Al₂O₃ catalyst containing SO₄²⁻ (black) using mixtures of NO and O₂ as an oxidising agent.

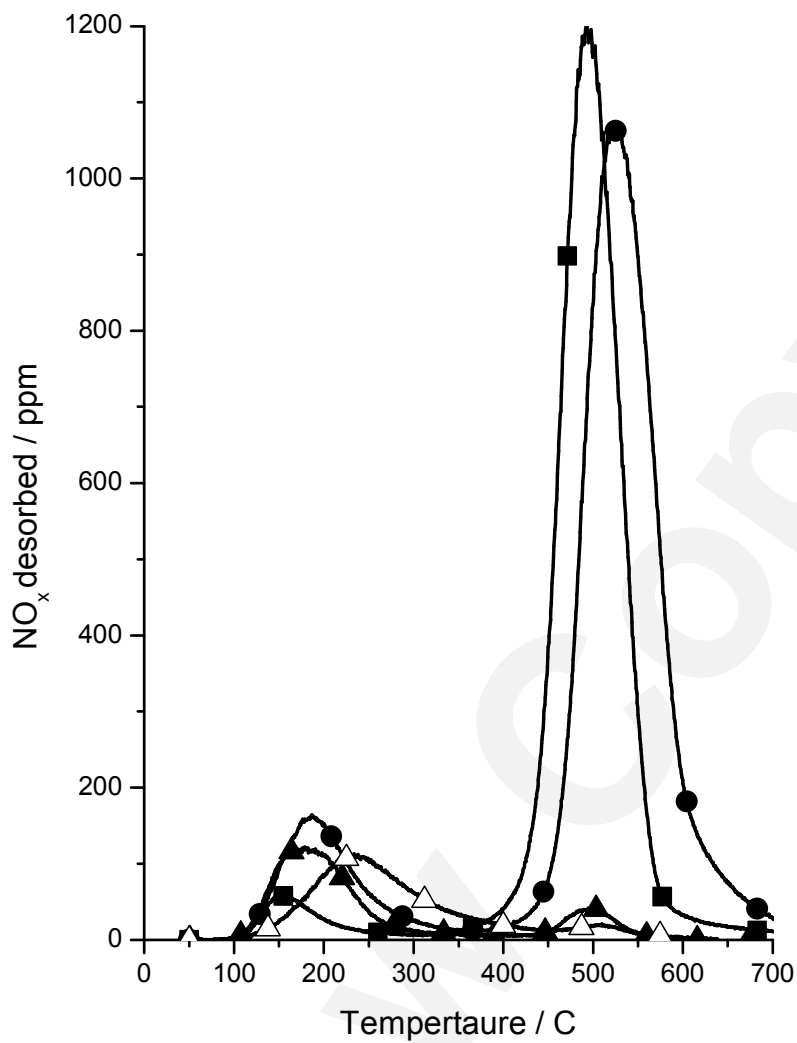


Figure 3. Temperature Programmed Desorption of NO_x from various Al₂O₃-supported catalysts. (■) Al₂O₃, (●), Na/Al₂O₃, (▲) Al₂O₃/S, (△)Na/Al₂O₃/S.