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Chemical deactivation of Ag/Al_2O_3 by sulphur for the selective reduction of NO_x using hydrocarbons

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Abstract

The hydrocarbon-SCR activity of Ag/Al_2O_3 catalysts is severely deactivated after low temperature (350 °C) sulphur ageing in the form of SO_2 exposure. Catalysts aged with SO_2, NO and hydrocarbon present accumulate a significantly larger amount of SO_4^{2-} than those aged in the presence of only O_2, H_2O and SO_2 when exposed to an equivalent amount of S. Following sulphation of the catalyst most of the sulphur can be removed by a high temperature (600 °C) treatment in the reaction gas. Regeneration in the absence of hydrocarbon is ineffective. The hydrocarbon-SCR activity of the sulphated catalyst using model hydrocarbons such as n-C_8H_{18} can be restored after a high temperature pre-treatment in the reaction gases. However this desulphation process fails to regenerate the hydrocarbon-SCR activity when diesel fuel is used in the activity test. TPR studies show that a major fraction of the sulphur species present in the catalyst is removed by such pre-treatment, but the slight residual amount of sulphur is sufficient to inhibit the activation of the diesel fuel on the Ag catalyst. The nature of the hydrocarbon species present for the hydrocarbon-SCR reaction and during the regeneration strongly influences the activity. In general aromatics such as C_7H_8 are less effective for reducing NO_x and regenerating the sulphated catalyst.

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Keywords: Hydrocarbon-SCR; Ag; NO_x; Sulphur poisoning

1. Introduction

The selective reduction of NO with hydrocarbons (HC-SCR) to reduce NO_x from diesel exhaust emissions has attracted considerable interest, and the subject has been extensively reviewed [1–8]. It probably represents one of the most challenging areas of environmental pollution control. Although many catalysts have been demonstrated to be effective for this reaction in the laboratory, the most effective catalysts are Pt/alumina, Cu exchanged ZSM5 and Ag/Al_2O_3, though a large variety of other Cu, zeolite and platinum group metal (pgm) based systems have also been studied. Ag/Al_2O_3 operates at higher temperatures and over a broad temperature range and has recently shown promise in vehicle testing [9,10]. A direct comparison of Cu/ZSM5 and Ag/Al_2O_3 showed their differences in activity and deactivation under simulated exhaust emission conditions [11]: thermal deactivation for Cu/ZSM5 due to Cu sintering and dealumination, coke deposition and sulphation for Ag/Al_2O_3. The activity of HC-SCR catalysts, particularly after long term ageing, has so far been insufficient to allow their commercial implementation [12].

We have studied this chemical poisoning by sulphur on a model Ag/Al_2O_3 system and simulated diesel vehicle exhaust using a wide range of model hydrocarbons and diesel fuels.

2. Experimental

The alumina support for the silver catalyst was γ-alumina with a surface area of ∼150 m^2/g. Ag catalysts with loadings of 2 and 4 wt.% were studied and they will be referred to as x% Ag/Al_2O_3 where x is the actual loading. The catalysts were prepared using traditional incipient wetness using silver nitrate as the precursor, and finally heated in air for 2 h at 500 °C. Catalysts were typically tested for HC-SCR activity by flowing 2 L/min gas over 0.4 g catalyst with a gas composition of 3000 ppm hydrocarbon (C_1 equivalent), 500 ppm NO, 5% CO_2, 600 ppm CO, 12% O_2, 5% H_2O, balance N_2. Experiments with diesel fuel used ultra low sulphur diesel fuel suitable for US

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2006 fuel regulations, with <10 ppm sulphur and a high aromatic content (~30%). The NO_x concentrations were measured using a chemiluminescence analyser (Signal). NO_x conversions were typically measured after 15 min at constant temperature starting from 200 °C and increasing the temperature in 50 °C intervals. We refer to this activity as the steady-state NO_x conversion.

Temperature programmed reduction (TPR) was carried out in 10% H_2/N_2 at a ramp rate of 10 °C/min, with H_2 consumption measured by thermal conductivity detector (TCD). The temperature programmed SO_2 desorption (SO_2 TPD) experiments were made by performing a temperature ramp at 10 °C/min from ambient temperature to 950 °C in N_2 (or 10% O_2/N_2 for temperature programmed oxidation) whilst monitoring the SO_2 evolution using an SO_2 analyser (ABB Automation Products).

3. Results and discussion

3.1. Deactivation by sulphur

Several authors have demonstrated the deactivation of Ag/Al_2O_3 system due to poisoning with SO_2 [13–16]. However, other authors have reported a promotional effect with SO_2 [17–19], with some describing a shift in the NO_x conversion window to higher temperature resulting in an increase in NO_x conversion at higher temperature but a reduced NO_x conversion at lower temperature [20,21]. Comparison of these papers is difficult as a wide range of catalysts and test conditions were employed. We have therefore looked at a range of parameters to distinguish their effect on the performance of Ag/Al_2O_3 on exposure to SO_2.

3.1.1. Effect of sulphation temperature

Fig. 1 shows the NO_x conversion for a 4% Ag/Al_2O_3 catalyst as a function of time, at 350 and 500 °C in the presence of 20 ppm SO_2, using *n*-octane as a model hydrocarbon. There was a constant NO_x conversion at 350 °C without SO_2. With SO_2 present at 350 °C, there was an initial small increase in NO_x conversion followed by a continuous decrease in NO_x conversion with time, showing rapid sulphur poisoning. When the ageing was done at 500 °C, the conversion increased slightly then stabilised. The effect of these two sulphur ageing temperatures on the activity window of the catalyst is shown in Fig. 2. The aged catalysts had similar temperature activity window profiles (steady state conditions with $n\text{-}C_8H_{18}$), with the low temperature NO_x conversion being severely suppressed but an improvement in the deNO_x activity above 450 °C. Therefore, depending on the temperature selected for the activity measurement, both an improvement and a reduction in NO_x conversion can be observed.

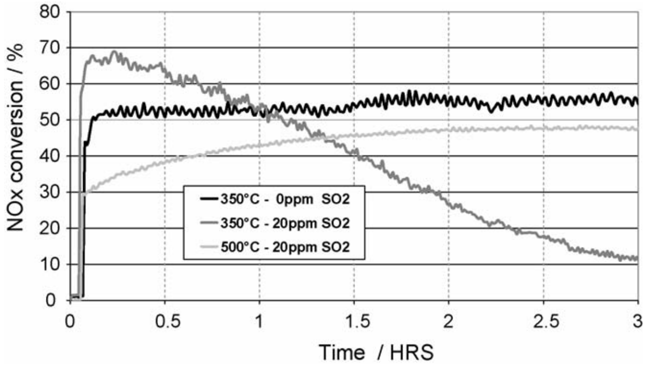

Fig. 1. NO_x conversion over 4% Ag/Al_2O_3 catalyst as a function of time at 350 and 500 °C in the full gas mixture in the presence of 20 ppm SO_2, 3000 ppm (C_1) *n*-octane.

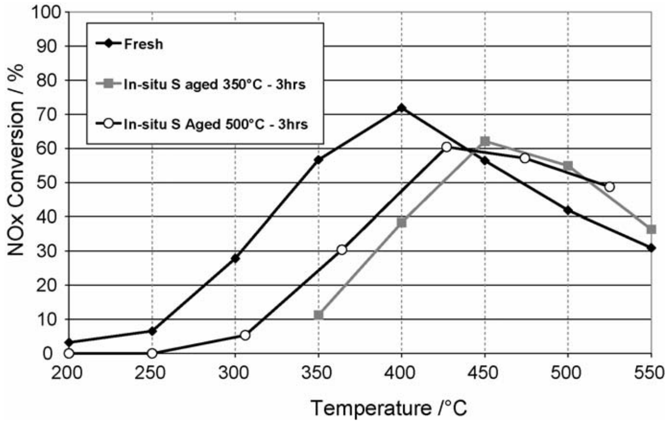

Fig. 2. Steady-state NO_x conversion as a function of temperature for fresh and aged 4% Ag/Al_2O_3 using *n*-octane. Ageing condition: 350 or 500 °C, 3 h, full gas mixture with 20 ppm SO_2, 2 g catalyst with 2 L/min flow rate.

The activity of the Ag/Al_2O_3 catalyst is stable under the reaction conditions when no SO_2 is present in the gas feed – Fig. 1. Moreover, this activity is reproducible: a second activity test performed on the same catalyst gave identical conversions. These results suggest that there is no permanent change in the catalyst under reaction conditions in the absence of SO_2. We attribute the decrease in the activity at low temperature (400 °C and below) to poisoning of the active sites for NO_x reduction, whilst the slight improvement in the high temperature (500–550 °C) activity following SO_2 ageing (and the initial increase in initial activity on ageing at 350 °C) can be associated with the poisoning of the metallic silver sites, which are unselective for HC-SCR, producing mostly total hydrocarbon combustion.

The amount of sulphur accumulated on the catalyst was evaluated by TPR. Analysis of the desorption products during TPR shows that hydrogen consumption and H_2S release coincide. This indicates that hydrogen consumption represents the reduction of sulphate formed by exposure to gas-phase sulphur. TPR analysis (not shown) of the 4% Ag/Al_2O_3 catalyst aged in situ in SO_2 at 350 or 500 °C showed that they have similar reduction profiles indicating they have been sulphated to a similar extent.

It seems likely therefore that the poisoning effect of sulphur can be attributed to sulphate formation around the active Ag sites leading to either simple site blocking or an electronic poisoning effect. However, this does not rule out some modifications of the Ag morphology during the sulphation. Changes in Ag morphology under reaction conditions have been reported previously [22].

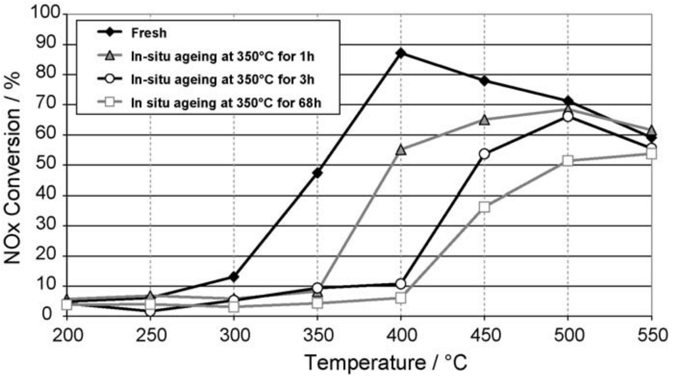

Fig. 3. Steady-state NO_x conversion as a function of temperature for fresh and aged 2% Ag/Al_2O_3 using *n*-octane. Ageing condition: 350 °C, 1, 3 or 68 h, full gas mixture with 20 ppm SO_2, 2 g catalyst with 2 L/min flow rate.

Table 1
Amount of sulphur adsorbed on 4% Ag/Al_2O_3 after exposure to different ageing atmospheres

Ageing	Hydrogen consumption (mmol/g)	S uptake (mg S/g catalyst)
Aged at 350 °C, NO, HC, H_2O, SO_2, air	3.27	10.5
Aged at 350 °C, NO, H_2O, SO_2, air	2.20	7.1
Aged at 350 °C, H_2O, SO_2, air	0.82	2.6

Ageing conditions: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 0 or 500 ppm NO, 0–3000 ppm (C_1) *n*-octane, balance air, 2 g catalyst with 2 L/min flow rate. Integration of the TPR peaks (Fig. 4) assuming $10H + S^{6+} \rightarrow S^{2-}$, i.e. $Ag_2SO_4 + 10H \rightarrow 2Ag + 4H_2O + H_2S$.

3.1.2. Catalyst formulation

Steady-state NO_x conversion data as a function of temperature for 2% Ag/Al_2O_3 fresh and aged at 350 °C are shown in Fig. 3. The light-off temperature of the sulphur aged catalysts was shifted towards higher temperature. It is interesting to note that for this lower silver loading, no improvement in the high temperature NO_x conversion was seen after sulphation, in contrast to the effect with 4% Ag/Al_2O_3. Both XPS and TEM analyses (results not shown) indicate that the 4% Ag/Al_2O_3 has a higher concentration of metallic Ag and larger Ag particles. This result suggests that for a higher loaded Ag catalyst containing more metallic Ag, sulphur can initially promote the high temperature NO_x conversion by poisoning the total oxidation activity, whilst for lower Ag loadings (where there is little or no metallic Ag) there is no improvement in high temperature NO_x conversion on sulphation.

3.1.3. Effect of gas composition

Angelidis and Kruse have demonstrated that the deactivation of the $Ag–Al_2O_3$ catalyst depends on the gas composition during sulphation [23]. Fig. 4 shows the TPR of a catalyst exposed to various ageing atmospheres. From this graph and the integration of the peaks in Table 1, it is clear that catalysts aged with SO_2 in the full reaction gas mixture (with NO and hydrocarbon present) accumulated a significantly larger amount of SO_4^{2-} than those aged in the presence of only O_2, H_2O and SO_2 when exposed to an equivalent amount of S. The rate of sulphation is much faster in the full reaction mixture, with the extent of sulphation increasing in the order of: full gas mixture > full gas mixture without hydrocarbon ≫ full gas mixture without NO and hydrocarbon ~ O_2, H_2O, SO_2. From Fig. 5 it is clear that the effect of NO is also to produce greater deactivation for HC-SCR activity after ageing. The dramatic effect of NO has been associated with its ability to oxidise SO_2 into SO_3 [23], which is more readily adsorbed on the $Ag–Al_2O_3$ catalyst. The SO_2 TPD given in Fig. 6 also showed the same trend as the TPR, with the catalyst aged in the presence of NO desorbing more sulphur. The presence of hydrocarbons also affects the amount of sulphates accumulated on the catalyst and thus the deactivation. A possible explanation could be the formation of sulphur containing organic compounds of the general type RSO_x [23].

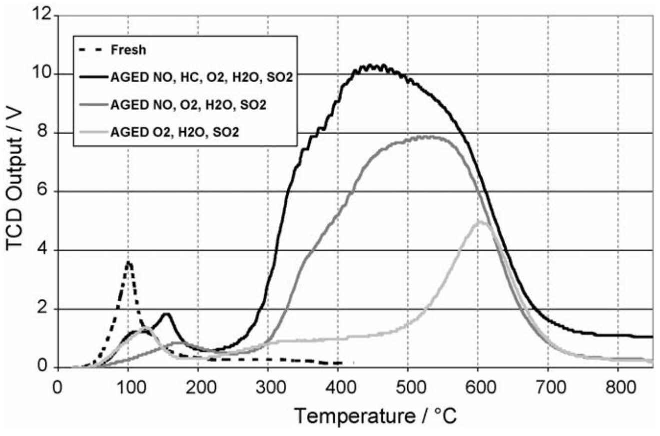

Fig. 4. TPR profile of a 4% Ag/Al_2O_3 sample fresh and aged under different atmospheres. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 0 or 500 ppm NO, 0–3000 ppm (C_1) *n*-octane, balance air, 2 g catalyst with 2 L/min flow rate.

Since NO has such an influence on the amount of sulphur accumulated of the catalyst, the following ageings have been done in the presence of NO in order to be closer to more realistic conditions. The Lean Hydrothermal Sulphur Ageing in

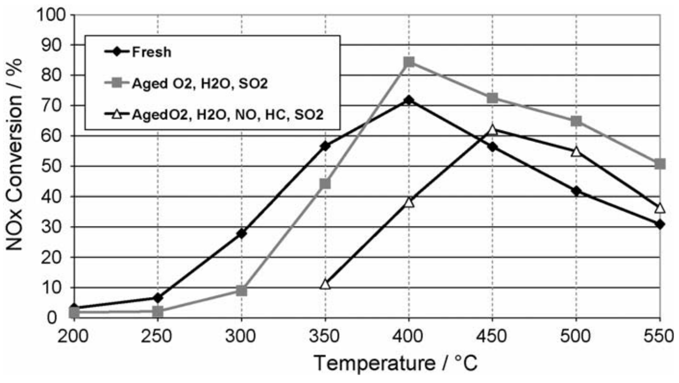

Fig. 5. Steady-state NO_x conversion as a function of temperature for fresh and aged 4% Ag/Al_2O_3 using *n*-octane. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 0 or 500 ppm NO, 0 or 3000 ppm (C_1) *n*-octane, balance air, 2 g catalyst with 2 L/min flow rate.

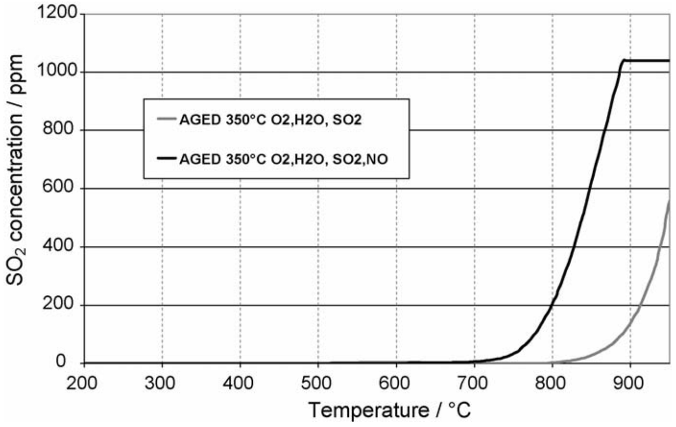

Fig. 6. SO_2 TPD of 4% Ag/Al_2O_3 sample aged under different atmospheres. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 0 or 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Note that the SO_2 analyser signal saturates for the sample aged in O_2, H_2O, SO_2 and NO when the desorption temperature reaches ~900 °C.

the presence of NO will be referred to as LHNSA, and the conditions are as follows: 350 °C, 68 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, to achieve an exposure of 120 mg S/g catalyst.

3.2. Regeneration

Clearly exposure to SO_2 can have a significant effect on NO_x conversion of Ag/Al_2O_3. One way to deal with this in a practical application might be to regenerate the catalyst periodically in situ. A number of previous studies have reported on attempts to regenerate sulphur poisoned Ag/Al_2O_3. Hickey et al. [24] showed that sulphated Ag/Al_2O_3 could not be regenerated by treatment at 450 °C in H_2. Meunier and Ross [14] showed that H_2 reduction could partially regenerate sulphated Ag/Al_2O_3 if higher temperatures were used and also that some regeneration could be achieved in the reaction test gas using propene as the reductant. Breen et al. [25] reported that a 2% Ag/Al_2O_3 catalyst could be almost fully regenerated when hydrogen was present in the regeneration mix.

3.2.1. Desulphation conditions

The SO_2 TPD of the sulphur aged 4% Ag/Al_2O_3 showed that sulphur does not decompose below 800 °C under N_2 – Fig. 6. A similar result was observed in an oxidising mixture of 10% O_2/N_2 (result not shown). Exposing a sulphur aged Ag/Al_2O_3 catalyst to this temperature or above to remove the sulphur under lean conditions would result in thermal deactivation [11,25]. This means that the sulphate species are too thermally stable under oxidising conditions and that a reductant needs to be present to remove the sulphur. Many studies have used hydrogen as the reductant [14,24,25], but it might be difficult to achieve, in an engine exhaust, the level of hydrogen required. Our approach was to use the hydrocarbons present for the test as reductant during the desulphation.

The TPR of a sulphur aged 4% Ag/Al_2O_3 catalyst exposed at 600 °C to various desulphation conditions is given in Fig. 7. When the desulphation was done in a model gas mixture containing N_2, O_2, H_2O and CO_2, all the sulphur accumulated on the catalyst during the ageing was still present after the regeneration step – Table 2. The change in the peak shape after the regeneration under those conditions suggests that there is some modification in the distribution of the sulphates on the surface, possibly associated with the high temperature exposure during the desulphation. However, most of the sulphur could be removed by a high temperature treatment in the reaction gas with hydrocarbons (*n*-octane) present due to sulphate reduction by the hydrocarbons. The corresponding NO_x conversion as a function of temperature is shown in Fig. 8. Regeneration in the absence of hydrocarbon was ineffective. The HC-SCR activity of the sulphated catalyst using model hydrocarbons such as *n*-octane could be restored after high temperature pre-treatment in the reaction gases.

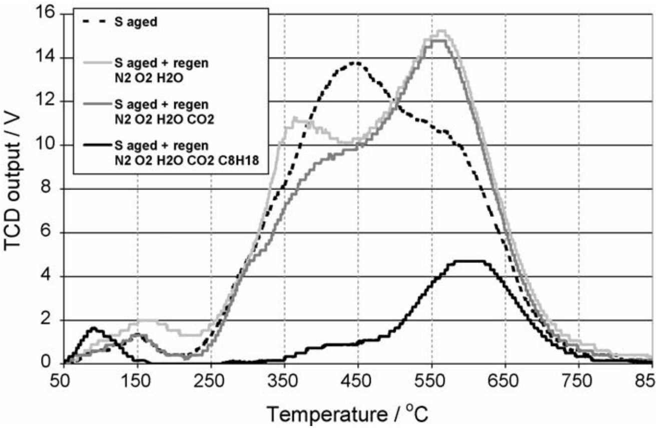

Fig. 7. TPR profile of a 4% Ag/Al_2O_3 sample aged and desulphated under different atmospheres. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Desulphation condition: 600 °C, 4.5% H_2O, 0 or 5% CO_2, 0 or 3000 ppm (C_1) *n*-octane, balance air.

The sulphation–desulphation procedure was repeated with toluene as the model hydrocarbon. Fig. 10 compares the HC-SCR activity of the aged 2% Ag/Al_2O_3 catalyst regenerated with either toluene or *n*-octane and shows that toluene was less effective for regenerating the sulphated catalyst. This partial

Table 2
Amount of sulphur adsorbed on 4% Ag/Al_2O_3 after regeneration under different atmospheres

Ageing	Hydrogen consumption (mmol/g)	S uptake (mg S/g catalyst)
S aged	4.4	14.1
Regeneration in N_2, O_2, H_2O	4.6	14.7
Regeneration in N_2, O_2, H_2O, CO_2	4.3	13.8
Regeneration in N_2, O_2, H_2O, CO_2, C_8H_{18}	1.0	3.1

Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Desulphation condition: 600 °C, 4.5% H_2O, 0 or 5% CO_2, 0 or 3000 ppm (C_1) *n*-octane, balance air. Integration of the TPR peaks (Fig. 7) assuming $10H + S^{6+} \rightarrow S^{2-}$, i.e. $Ag_2SO_4 + 10H \rightarrow 2Ag + 4H_2O + H_2S$.

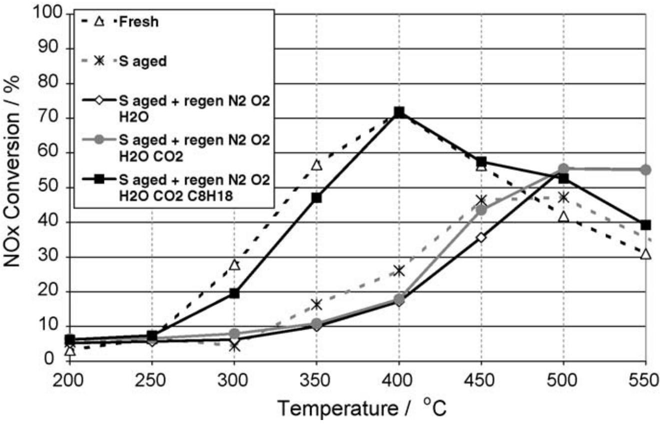

Fig. 8. Steady-state NO_x conversion as a function of temperature for fresh, aged and desulphated 4% Ag/Al_2O_3 using *n*-octane. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Desulphation condition: 600 °C, 4.5% H_2O, 0 or 5% CO_2, 0 or 3000 ppm (C_1) *n*-octane, balance air.

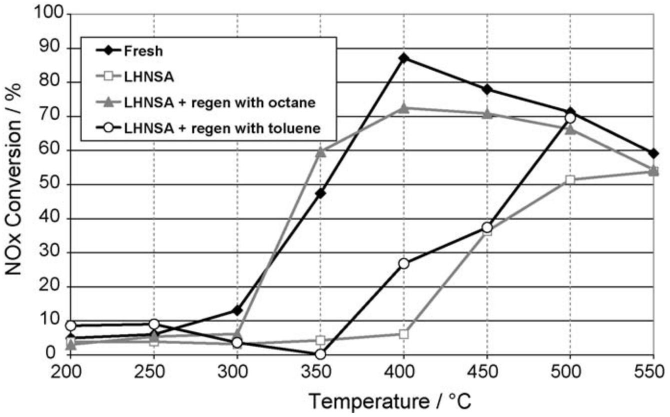

Fig. 10. Steady-state NO_x conversion as a function of temperature for fresh, aged and desulphated 2% Ag/Al_2O_3 using *n*-octane. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Desulphation condition: 600 °C, full gas mixture, 3000 ppm (C_1) as *n*-octane or toluene.

regeneration could be linked to the amount of sulphur left on the catalyst, which was significantly higher for the 2% Ag/Al_2O_3 regenerated with toluene – Fig. 9. Toluene is known to be less effective at reducing NO_x [25]. Results in our laboratory have shown no activity below 450 °C and a maximum NO_x conversion of 30% at 500 °C, which matches the temperatures at which the hydrocarbons are activated. The fact that toluene is more difficult to activate than octane could explain its lower efficiency in the desulphation.

3.2.2. *Effect of sulphation–desulphation on the SCR activity in diesel fuel*

Figs. 8 and 10 both show that independent of the catalyst formulation, good recovery of the HC-SCR activity in model hydrocarbons can be achieved. The NO_x conversion in diesel fuel of 2% Ag/Al_2O_3 catalysts fresh, after sulphur ageing and desulphation with model hydrocarbons present in the gas feed is given in Fig. 11. It is worth noting that the light-off temperature of the Ag catalyst tested with diesel fuel occurs at much higher temperature than when the test was performed with model hydrocarbons such as *n*-octane. This effect has been associated with coking [11] and although it is reversible by exposure at high temperature, it leads to low temperature (<450 °C) deactivation. Only partial recovery of the SCR activity was noticed after desulphation. TPR studies showed that a major fraction of the sulphur species present in the catalyst was removed by such pre-treatment, but the slight residual amount of sulphur was sufficient to inhibit the activation of the diesel fuel on the Ag catalyst. Diesel fuel, which is a complex mix of different types of hydrocarbons, is much more difficult to activated than long chain alkanes as octane for example, which can explain why diesel fuel is less effective as a SO_x removal agent.

Recent results in this laboratory have shown that a complete regeneration with model hydrocarbons can be achieved with more aggressive conditions than those shown here, though without thermal deactivation of the catalyst, leading to a complete recovery of the activity in diesel fuel [26].

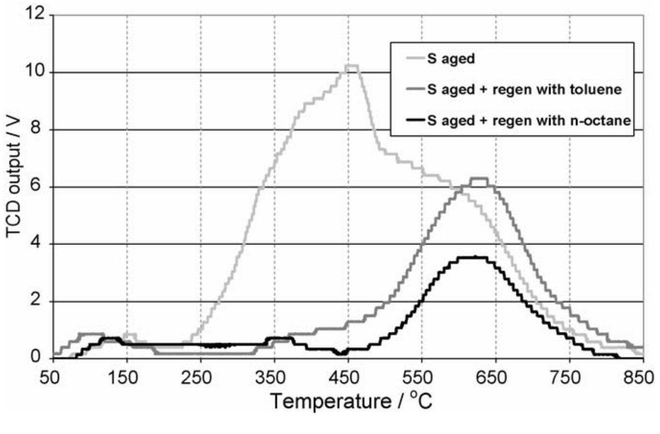

Fig. 9. TPR of aged and desulphated 2% Ag/Al_2O_3. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Desulphation condition: 600 °C, full gas mixture, 3000 ppm (C_1) as *n*-octane or toluene.

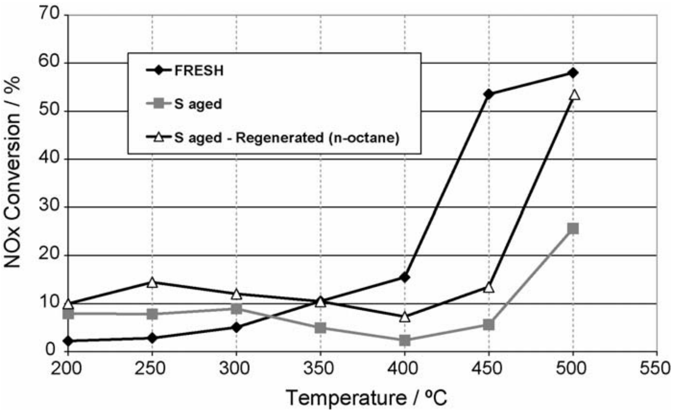

Fig. 11. Steady-state NO_x conversion as a function of temperature for fresh, aged and desulphated 2% Ag/Al_2O_3 using diesel fuel. Ageing condition: 350 °C, 3 h, 20 ppm SO_2, 4.5% H_2O, 500 ppm NO, balance air, 2 g catalyst with 2 L/min flow rate. Desulphation condition: 600 °C, full gas mixture, 3000 ppm (C_1) *n*-octane.

4. Conclusions

The deactivation of Ag/Al_2O_3 catalysts by sulphur depends on a number of factors:

- Catalyst formulation: for a high loaded Ag catalyst containing more metallic Ag, sulphur can initially promote the high temperature NO_x conversion by poisoning the total oxidation activity. However, for all Ag/Al_2O_3 catalysts, the low temperature NO_x conversion was suppressed.
- Gas mixture composition: the catalysts aged with SO_2, NO and hydrocarbon present accumulated a significant larger amount of SO_4^{2-} than those aged in the presence of only O_2, H_2O and SO_2 when exposed to an equivalent amount of sulphur.

The HC-SCR activity of a sulphated catalyst could be recovered when the catalyst was exposed at high temperature under lean conditions in the presence of hydrocarbons. Toluene was less effective for regenerating the sulphated catalyst than *n*-octane. When the catalyst desulphated with model hydrocarbons was tested in diesel fuel, only partial recovery of the activity was achieved. A major fraction of the sulphur species present in the catalyst was removed by the pre-treatment, but the slight residual amount of sulphur was sufficient to inhibit the activation of the diesel fuel on the Ag catalyst. A complete regeneration with model hydrocarbons could be achieved with more aggressive conditions leading to a complete recovery of the activity in diesel fuel.

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