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Controlling the Sulfur Poisoning of Ag/Al₂O₃ Catalysts for the Hydrocarbon SCR Reaction by Using a Regenerable SOₓ Trap.

Sarayute Chansai*, Robbie Burch and Christopher Hardacre

CenTACat, School of Chemistry and Chemical Engineering, Queen’s University Belfast, David Keir Building, Belfast BT9 5AG, N. Ireland, U.K.

* Corresponding Author: s.chansai@qub.ac.uk (Tel.: +44(0) 28 9097 4462)

Abstract

The deactivation of a silver-based hydrocarbon selective catalytic reduction catalyst by SOₓ and the subsequent regeneration under various operating conditions has been investigated. Using a sulfur trap based on a silica-supported catalyst it was found that, for a Ag/SiO₂ + Ag/Al₂O₃ combination, the negative effect of SO₂ on the n-octane-SCR reaction can be eliminated under normal operating conditions. The trap can be regenerated by hydrogen at low temperatures or at higher temperatures using a hydrocarbon reductant.

Keywords: Ag catalysts, NOx reduction, SOₓ trap, n-octane, HC-SCR, Regeneration
Introduction

Lean-burn diesel engines offer significant fuel efficiency advantages as compared with stoichiometric gasoline engines. However, in diesel engines nitrogen oxides (NO\textsubscript{x}) are produced in the presence of a large excess of oxygen. This creates a problem for the reduction of NO\textsubscript{x} under oxidising conditions, causing air pollution. One of the promising approaches to eliminate NO\textsubscript{x} is to use the selective catalytic reduction (SCR) with hydrocarbons (HC-SCR) using silver-based catalysts [1-24]. It is well-known, however, that sulphur oxides (SO\textsubscript{x}) are detrimental to the HC-SCR activity on Ag catalysts at temperatures between about 300 and 500 °C [5, 11-24].

Recent research by Li and King [25] has shown that SO\textsubscript{2} can be efficiently trapped on Ag/SiO\textsubscript{2} catalysts over a wide range of temperatures (300 – 550 °C) under lean conditions. Moreover, these materials can be completely regenerated by a CO/CO\textsubscript{2}/C\textsubscript{3}H\textsubscript{6}/H\textsubscript{2} mixture during rich cycles at the same temperature. This is very interesting because Ag/Al\textsubscript{2}O\textsubscript{3} deactivated by SO\textsubscript{2} can also be regenerated under rich conditions at high temperatures [5, 13, 17, 18]. Therefore, the use of Ag/SiO\textsubscript{2} as a SO\textsubscript{2} absorbent upstream of Ag/Al\textsubscript{2}O\textsubscript{3} during the HC-SCR reaction at intermediate temperatures (i.e. ca. 300 – 500 °C) could be a practical way to protect the HC-SCR catalyst. In this study, we have investigated the efficacy of SO\textsubscript{2} trapping and regeneration (RG) on HC-SCR activity using a double bed system. In addition, we have investigated appropriate regeneration conditions needed to reactivate any deactivated Ag catalysts.

2. Experimental

2.1 Catalyst Preparation

The Ag/Al\textsubscript{2}O\textsubscript{3} catalyst, obtained from Johnson Matthey plc, was prepared by impregnation of γ-Al\textsubscript{2}O\textsubscript{3} (LaRoche Industries Inc.). The Al\textsubscript{2}O\textsubscript{3} support material was ground to a particle size of < 250 μm and mixed with a solution containing 0.022 M AgNO\textsubscript{3}. The catalyst was then filtered, dried at room temperature for 24 h and further dried at 100 °C for 3 h, after which the catalyst was calcined at 550 °C for 3 h [10]. For the preparation of the SO\textsubscript{2} trap material the Ag/SiO\textsubscript{2} catalyst was prepared by incipient wetness impregnation of the SiO\textsubscript{2} support using AgNO\textsubscript{3}. The resulting catalyst was then dried at 100 °C overnight and then calcined at 550 °C for 4 h. Although Li and King [25] have reported that there is no significant effect of Ag loadings between 2.5 and 10% on SO\textsubscript{x} trap performance, 5% Ag loading show the highest performance. Therefore, 5% wt of Ag/SiO\textsubscript{2} was used in this study. The Ag content of the catalyst was determined by the Direct Current Plasma method to be approximately 2 wt% and 5 wt% Ag, and the BET specific surface areas of the catalysts were 170 m\textsuperscript{2} g\textsuperscript{-1} and 293 m\textsuperscript{2} g\textsuperscript{-1} for Ag/Al\textsubscript{2}O\textsubscript{3} and Ag/SiO\textsubscript{2}, respectively.

2.2 SO\textsubscript{2} deactivation, trap and regeneration

The catalytic performance of both Ag catalysts was measured in a fixed-bed flow reactor system consisting of a quartz reactor tube. The catalysts were held in place between plugs of quartz wool and a K-type thermocouple was placed in the centre of each catalyst bed. Single and dual catalyst beds with separate furnaces were used in this study. The 5% Ag/SiO\textsubscript{2} catalyst was placed upstream of the 2% Ag/Al\textsubscript{2}O\textsubscript{3} catalyst. The gap between both Ag beds was ca. 50 cm. Each of the gases in the feed system was controlled individually by mass flow controllers, while n-octane and water vapour were introduced to the system by means of separate saturators with Ar as a
carrier gas. The n-C8H18 saturator was placed in an ice/water bath where its temperature was carefully controlled while the temperature of the H2O saturator was controlled using a thermostatic bath. All the lines following the water saturator were heated to prevent condensation. The feed gas stream consisted of NO, C8H18, O2, H2O, CO2, H2, SO2 and Ar balance. The total gas flow rate was 276 cm³ min⁻¹ over 276 mg of each Ag catalyst which was sieved to obtain particle sizes between 250 and 450 μm. The inlet and outlet NOx concentrations were determined by a Signal 4000VM series chemiluminescence detector. In these studies, total NOx conversion is defined as NOx reduction to N2 and N2O.

Several different gas mixes were used as follows.

GM1: 720 ppm NO; 4340 ppm (as C1) C8H18; 4.3% O2; 7.2% CO2; 7.2% H2O

GM2: 720 ppm NO; 4340 ppm (as C1) C8H18; 4.3% O2; 7.2% CO2; 7.2% H2O; 1-30 ppm SO2

RGM1: 720 ppm NO; 4340 ppm (as C1) C8H18; 7.2% CO2; 7.2% H2O; 1-30 ppm SO2; 2% H2

RGM2: 720 ppm NO; 4340 ppm (as C1) C8H18; 7.2% CO2; 7.2% H2O; 1-30 ppm SO2; 16000 ppm C8H18 (as C1)

RGM3: 720 ppm NO; 4340 ppm (as C1) C8H18; 7.2% CO2; 7.2% H2O; 0.5% O2; 1-30 ppm SO2; 16000 ppm C8H18 (as C1)

The SCR activity of the Ag catalysts was investigated as a function of time on stream at 350 °C without the presence of SO2 (using gas mixture GM1) for 15 h in order to obtain the baseline of NOx conversion. SO2 was then added to the SCR gas mix (GM2) with different concentrations of SO2 for 15 h to examine whether or not deactivation had taken place for both single Ag/Al2O3 and dual Ag/SiO2 and Ag/Al2O3 catalyst beds. In order to prevent a saturation of adsorbed SOx on the Ag catalysts, the regeneration process was carried out at 550, 600 or 650 °C for 1 or 5 min under different regeneration mixes using the procedure outlined in Figure 1. NOx conversions were measured at 350 °C under GM2 after 3 h of each regeneration step when using 30 ppm SO2 and after 6 h when using 1, 5 or 10 ppm SO2 in the SCR feed.

2.3 Temperature-programmed reaction (TPR)

The SO2-TPR experiments were carried out to investigate the desorption properties of adsorbed SOx on 5% Ag/SiO2. Prior to the measurements, 276 mg of 5% Ag/SiO2 catalyst was exposed to GM2 consisting of 720 ppm NO, 4340 ppm (as C1) C8H18, 4.3% O2, 7.2% CO2, 7.2% H2O, 10 ppm SO2 and Ar balance at 350 °C for 6 h. The total flow rate was 276 cm³ min⁻¹. The resulting Ag catalyst was then used for SO2-TPR measurements. Approximately 50 mg of SO2-pretreated Ag/SiO2 catalyst was exposed to different gas regeneration mixes (RGMx without SO2) with a total flow rate of 100 cm³ min⁻¹ for 15 min at 100 °C before increasing the temperature up to 750 °C at a rate of 10 °C/min. Desorbed H2S, COS and SO2 species were monitored by a Hiden Analytical HPR20 quadrupole mass spectrometer.

3. Results and Discussion

3.1 The effect of SO2
Figure 2 shows the effect of exposure to SO$_2$ on the Ag/Al$_2$O$_3$ catalyst under SCR gas mix (GM$_2$) containing 5 ppm SO$_2$ for a period of 15 h at different temperatures. It is clearly seen that only a very small amount of deactivation was observed at 550 °C after 15 h with 5 ppm SO$_2$ in the SCR gas mix. However, at any of the lower temperatures tested, there was severe deactivation over a period of 6-15 h with the NOx conversion decreasing to zero. Please note that the catalytic activity tests under SCR gas mix (GM$_1$) were also performed over Ag/SiO$_2$ on its own and NOx conversions of ca. 1% (not shown) were observed at 300 and 350 °C. This is consistent with the research work by Bethke and Kung [26] that Ag/SiO$_2$ has very poor SCR activity with propene at 400 °C (8% NO conversion to only N$_2$O).

To investigate the effect of the SO$_2$ trap, both single Ag/Al$_2$O$_3$ and dual Ag/SiO$_2$ and Ag/Al$_2$O$_3$ catalysts were exposed to the SCR gas mix with and without SO$_2$ as shown in Figure 3. Prior to the addition of SO$_2$ into the SCR feed, the catalytic activity (Fig. 3a, dashed line) was very stable and there was no deactivation observed over 15 h. However, there is a small decrease in NOx conversion from 89 to 67% when adding 1 ppm SO$_2$ into the SCR gas mix. Figure 3a also shows the negative effect of SO$_2$ on the SCR activity of the Ag/Al$_2$O$_3$ catalyst, which deactivated significantly when exposed to 5, 10 or 30 ppm SO$_2$ over the course of experiments at 350 °C, showing decrease in NOx conversions from ca. 90 to 0%. Although the fact that deactivation of Ag/Al$_2$O$_3$ catalyst by SO$_2$ was reported in many papers, the deactivated catalysts could not easily be regenerated [5, 13, 17, 18].

It is, therefore, very interesting to see the effect of using the SOx trap to protect the Ag/Al$_2$O$_3$ bed when this was tested using an octane-SCR mixture (GM$_2$). Of course, without a regeneration process, saturation of the Ag/SiO$_2$ catalyst will eventually result in deactivation of the Ag/Al$_2$O$_3$. Figure 3(b) shows that this only occurs after about 6 h on stream when using 10 ppm of SO$_2$ which can be compared with much less than 1 h without the SOx trap in place.

3.2 The effect of regeneration

Prior to the saturation of Ag/SiO$_2$ by adsorbed SO$_x$ the effect of regeneration was investigated by exposing both Ag/SiO$_2$ and Ag/Al$_2$O$_3$ catalysts to different regeneration gas mixes at three different temperatures. Note that above 550 °C the deactivation of Ag/Al$_2$O$_3$ by SO$_2$ does not occur (Figure 2).
Figure 4 shows the profiles of SO$_2$ released into the gas phase during temperature-programmed reduction under different gas mixes. Note that no H$_2$S and COS was observed to be released from the Ag/SiO$_2$ catalysts (not shown). Using gas mixture RGM$_1$ containing hydrogen we observe a remarkable regeneration of the Ag/SiO$_2$ at temperatures between 200 and 400 °C which can be contrasted with the profile obtained using a 5% O$_2$/Ar feed. Figure 4 also shows that the octane in the absence of hydrogen is much less effective at regenerating the Ag/SiO$_2$ SO$_x$ trap. This is consistent with the literature [5, 17, 18, 25] which reports that heating in the presence of H$_2$ could almost fully regenerate deactivated Ag catalysts. The effect of the most favourable regeneration conditions (RGM$_1$) is shown in Figure 5. For both single Ag/Al$_2$O$_3$ and dual Ag/SiO$_2$ +Ag/Al$_2$O$_3$ beds, the initial NO$_x$ conversion on fresh samples over a period of 15 h under gas mixture GM$_1$ was ca. 89%. In the absence of the Ag/SiO$_2$ trap, as expected, deactivation of the Ag/Al$_2$O$_3$ catalyst is severe (Please note that SO$_2$ was never removed from the feed once introduced into the SCR gas mix). After 1 min regeneration under RGM$_1$ at 550 °C, the SCR activity observed over a period of 6 h under GM$_2$ was very poor. On the other hand, when using Ag/SiO$_2$ upstream as a SO$_x$ trap, there was very little deactivation. The decrease in NO$_x$ conversion was only 2% over the course of 48 h. The SCR activity on the downstream Ag/Al$_2$O$_3$ after the third time of regeneration was equally high, giving a NO$_x$ conversion of ca. 87%.

The effect of regeneration was probed using RGM$_1$ containing small amount of octane and 2% H$_2$ at 550 °C for 1 and 5 min. Figure 6 compares the effect exposure to different concentrations of SO$_2$. For 1 or 5 ppm, it was found that, as expected, the regeneration is very high even after a total exposure of 27 h before the third regeneration. NO$_x$ conversions in both cases were maintained above 85%. In contrast, at the very high concentrations of 10 or 30 ppm of SO$_2$ the trapping by the Ag/SiO$_2$ is not complete and progressive deactivation of the Ag/Al$_2$O$_3$ occurs. However, for a normal low sulphur diesel fuel, with a sulphur level below 10 ppm, the concentration of SO$_2$ in the exhaust would be < 1 ppm and the results in Figure 6 show that, under those conditions, we can achieve excellent protection of the silver HC-SCR catalyst.

Figure 7 compares the different regeneration mixtures, with or without hydrogen and at different temperatures. Overall, although the presence of hydrogen is very favourable, good regeneration can be achieved in the absence of hydrogen by using higher temperatures and/or longer regeneration times.

Conclusions

SO$_2$ deactivation and regeneration has been investigated over dual Ag/SiO$_2$ + Ag/Al$_2$O$_3$ catalytic systems. It was found that the negative effect of SO$_2$ on the $n$-octane-SCR of NO$_x$ reaction over a Ag/Al$_2$O$_3$ catalyst can be almost eliminated when using Ag/SiO$_2$ as a SO$_x$ trap material.

Acknowledgements

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References

Figures and Captions

**Figure 1** Experimental protocols for the regeneration of 5% Ag/SiO$_2$ and 2% Ag/Al$_2$O$_3$ during octane-SCR of NO$_x$ at 350 °C.
Figure 2 NOx conversion as a function of time of exposure to the gas mix containing 5 ppm SO2 (GM2), at 300, 350, 400, and 550 °C. Feed conditions (GM2): 720 ppm NO, 4340 C8H18 (as C1), 4.3% O2, 7.2% CO2, 7.2% H2O, 5 ppm SO2 and Ar balance.
Figure 3 NO\textsubscript{x} conversion as a function of time exposed to different concentrations of SO\textsubscript{2} (1-30 ppm) during octane-SCR of NO\textsubscript{x} reaction at 350 °C over (a) single 2% Ag/Al\textsubscript{2}O\textsubscript{3} and (b) 5% Ag/SiO\textsubscript{2} placed upstream of 2% Ag/Al\textsubscript{2}O\textsubscript{3}. Feed conditions (GM\textsubscript{2}): 720 ppm NO, 4340 C\textsubscript{8}H\textsubscript{18} (as C1), 4.3% O\textsubscript{2}, 7.2% CO\textsubscript{2}, 7.2% H\textsubscript{2}O, 5 ppm SO\textsubscript{2} and Ar balance.
Figure 4 The profiles of desorbed SO$_2$ during temperature-programmed reactions using different regeneration mixes (RGM$_x$) without SO$_2$ over 5% Ag/SiO$_2$. Prior to these measurements, Ag/SiO$_2$ (276 mg) was exposed to GM$_2$ with 10 ppm SO$_2$ at 350 $^\circ$C for 6 h.
Figure 5 The effect of exposure to 5 ppm SO₂ at 350 °C and a 1 min regeneration time at 550 °C in rich conditions (RGM₁) containing 720 ppm NO, 542 ppm n-C₈H₁₈, 2% H₂, 5 ppm SO₂, 7.2% CO₂, 7.2% H₂O. All NOₓ conversions were obtained at 350 °C after 15 h in gas mix GM₁ for fresh samples, and after 15 h under GM₂ (with SO₂ present) and then after 6 h under GM₂ after each regeneration step.
Figure 6 The effect of exposure to different concentration of SO₂ at 350 °C and (a) 1 min and (b) 5 min regeneration at 550 °C in rich conditions (RGM₁) containing 720 ppm NO, 542 ppm n-C₈H₁₈, 2% H₂, 5 ppm SO₂, 7.2% CO₂, 7.2% H₂O. All NOₓ conversions were obtained at 350 °C at different times depending on the concentrations of added SO₂. Please refer to experimental section (Fig. 1) for details.
Figure 7 The effect of (a) 1 min and (b) 5 min regeneration using different mixes (RGM1, RGM2, and RGM3) at 550, 600 or 650 °C. All NOx conversions were obtained at 350 °C after 15 h in gas mix GM1 for fresh samples, and after 15 h under GM2 (with 5 ppm SO2 present) and then after 6 h under GM2 after each regeneration step. Please refer to the experimental section (Fig. 1) for details.