

Experiment Report Form

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- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Investigation of structure and evolution of active silver species in Ag/Al₂O₃ catalysts for NO_x abatement

Experiment number:
CH-3769

| | | |
|---------------------------|---|--|
| Beamline: BM01B | Date of experiment: from: 03.07.2013 to: 08.07.2013 | Date of report: <i>Received at ESRF:</i> |
| Shifts: 15 | Local contact(s): Wouter Van Beek | |

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Report:

Introduction

Selective reduction of NO_x by NH₃ is the most widely used technique for the removal of nitrogen oxides from the exhaust of diesel vehicles and power plants. Ag/Al₂O₃ catalysts are a promising alternative for the currently used zeolites and vanadia-containing catalysts due to their high activity with different reducing agents and high thermal stability [1]. However, currently, the structure – activity relationship for the Ag/Al₂O₃ catalysts is not understood. Furthermore, there is a debate on the mechanism of the sulfur poisoning of these catalysts. This motivated us to carry out a synchrotron study of Ag/Al₂O₃ calcination (as the important part of the preparation process) and a study of reducibility of different Ag/Al₂O₃ catalysts to correlate their structure with their activity. Part of this study has been published in the paper “Ti and Si doping as a way to increase low temperature activity of sulfated Ag/Al₂O₃ in H₂-assisted NH₃-SCR of NO_x” [2].

Experimental

The catalysts were prepared by incipient wetness impregnation of the home-made γ -alumina ($S_{\text{BET}}=298 \text{ m}^2/\text{g}$) and SASOL Siralox 5/230 (5 mol.% SiO₂ : 95 mol.% Al₂O₃, $S_{\text{BET}}=292 \text{ m}^2/\text{g}$) with the corresponding amount of AgNO₃ to get Ag loading of 1 – 6 wt%. After impregnation all catalysts were dried overnight and calcined at 550 °C for 4 hours in static air. Portion of 6%Ag/Al₂O₃ and 6%Ag/Siralox catalysts was presulfated by impregnating with NH₄SO₃, drying and calcination as described elsewhere [1]. Presulfated catalysts are designated as 6%Ag/Al₂O₃^{sulf} and 6%Ag/Siralox^{sulf}. For catalytic measurements the catalysts were pressed, crushed and sieved to obtain the fraction 0.18 – 0.35 mm and for the synchrotron study – 0.1 – 0.2 mm.

The synchrotron XRD and EXAFS study was performed on Swiss-Norwegian Beamline (BM01B) of the ESRF. For combined XRD and XANES / EXAFS during temperature programmed reduction (TPR) two

catalysts Ag/Al₂O₃ and Ag/Siralox were placed in 1.5 mm quartz capillaries with 0.01 mm thick walls (approx. 1 cm bed length, 7 mg of a catalyst, sieve fraction 0.1 – 0.2 mm). Si (111) double crystal monochromator was used for energy selection during the X-ray absorption measurements and the beam size was kept 0.5x3 mm. The capillary was placed in the X-ray beam above a hot air blower (Oxford GSB-1300). The catalysts were heated from 20 to 480°C with a ramp rate of 5 K/min under flow of 5% H₂/He (50 ml/min). X-ray absorption spectra were recorded in transmission geometry with Ag foil used as a standard. Spectra were treated and linear combination analysis was done by using Athena software [3]. For the Fourier transform k³-weighing and 2 – 14 Å Hanning-type window was used. The relative contributions of the formed species were quantified by linear combination fitting (LCF) of XANES spectra using the Athena software in the range from -10 to 30 eV relative to the threshold energy. The energy was fixed during LCF. XRD patterns were recorded using Si (111) channelcut monochromator and a 2D CMOS (Dexela) detector and converted to XY-format using FIT2D software from ESRF. The beam size for XRD was 1x1 mm and the exact X-ray wavelength (0.50527 Å) was determined by measuring LaB₆ reference.

Results

Calcination of AgNO₃/Al₂O₃ containing 6%Ag (in the flow of air, up to 550 °C with 5 °C/min ramp) was followed by in-situ XAS and XRD techniques. QEXAFS did not show the change in the Ag sites structure or environment. XRD spectra in the beginning and in the end of a calcination are shown on Fig. 1. No reflections from AgNO₃ can be seen in both cases which together with the fact that AgNO₃ is seen by the laboratory X-ray diffractometer (unpublished results) suggest AgNO₃ decomposition under the X-ray beam already at 20 °C, i.e. beam damage. The reflections at 2θ = 12.3° and 23.7° (ascribed to metallic Ag) disappear between 250 and 300 °C (Fig. 2) which may be due to Ag redistribution or because of the increased thermal disorder.

The as-calcined sample was later used to monitor the changes in the Ag/Al₂O₃ catalyst under the model gas mixture containing 1000 ppm H₂ and 5% O₂ in He. The goal was to mildly reduce the catalyst by a small amount of H₂ under net-oxidizing working conditions to estimate the size of active Ag particles. This model models net-oxidizing conditions of the diesel exhaust and the two mentioned gases are proposed to react with Ag with the production of peroxide anions further activating NO_x [4]. EXAFS scans were recorded at 20 °C and between 150 and 550 °C (100 °C steps). The obtained spectra, however did not reveal any significant catalyst reduction taking place. Hence, the Ag/Al₂O₃ catalysts with different activity were reduced during the in-situ TPR-XAS.

At first, 1, 4, and 6%wt Ag/Al₂O₃ catalysts were studied as having the biggest differences in activity [5]. 1%Ag/Al₂O₃ showed slower reduction and in the case of 6%Ag/Al₂O₃ the reduction started already at 20 °C. Shift of Ag reduction to lower temperatures have been observed previously with increase of Ag content and was ascribed to a formation of bigger Ag_xO_y clusters [6]. FT EXAFS of the reduced catalysts demonstrated higher coordination numbers (bigger particles) for 4 and 6%Ag/Al₂O₃ than for 1%Ag/Al₂O₃, however, there was hardly any difference in the EXAFS and XRD spectra of all studied Ag/Al₂O₃, 4% and 6% Ag, even for 6%Ag/Al₂O₃ and 6%Ag/Siralox which are very different in terms of catalytic activity. Fig. 3 shows the relative concentrations of Ag⁰ species as obtained by the linear combination analysis of XANES spectra

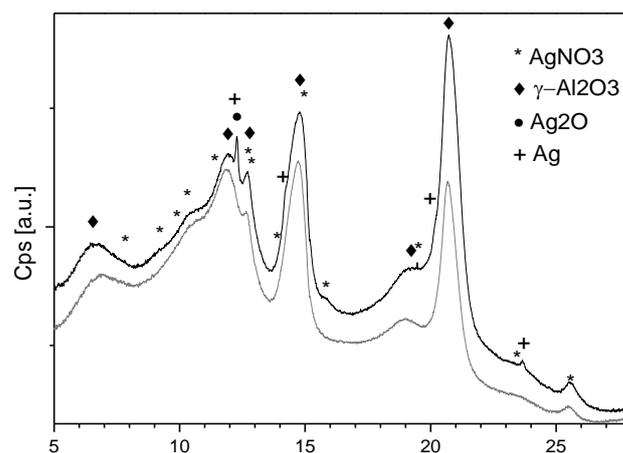


Fig. 1. XRD patterns measured before (black) and after (gray) calcination of AgNO₃/Al₂O₃ at 20 °C and at 550 °C during calcination in synth. air.

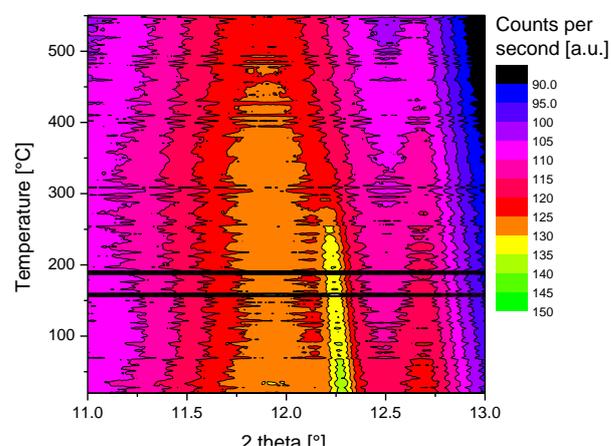


Fig. 2. XRD pattern measured during the calcination of AgNO₃/Al₂O₃. The reflex from metallic Ag⁰ (2θ = 12.3°) disappears between 250 and 300 °C.

the linear combination analysis of XANES spectra

measured in the course of TPR. 6%Ag/Al₂O₃ starts reducing already at room temperature as shown in Fig. 3. 6%Ag/Siralox has lower reducibility but is more active which can be explained by higher Ag dispersion in this case [2]. Low loaded 4%Ag/Al₂O₃ reduces with approximately the same rate as 6%Ag/Siralox which points out similar Ag dispersion, and 1%Ag/Al₂O₃ requires even higher reduction temperature. Therefore, the reducibility of Ag/Al₂O₃ catalysts, as derived from TPR-XAS, was main and only marker which can be correlated with the catalytic activity of Ag/Al₂O₃. XRD scans performed before the temperature ramp showed higher intensity of reflections of Ag⁰ [2] whereas final XRD patterns showed the same large Ag⁰ particles for all studied 6%Ag-containing catalysts [supplementary material for ref. 2].

Last but not the least sulfur-poisoned samples 6%Ag/Al₂O₃^{sulf} and 6%Ag/Siralox^{sulf} have been compared with their fresh counterparts by means of EXAFS, XRD and TPR-XAS. No differences was found neither in structure of Ag sites, nor in the reducibility of Ag. This supports our earlier conclusion of SO_x mainly adsorbing on the alumina support but not on the Ag [1].

Conclusions

EXAFS, XANES and XRD were used *in-situ* for the thorough multifaceted characterisation of Ag/Al₂O₃ catalysts during calcination, under a gas feed modelling catalytic feed and during TPR with hydrogen.

In-situ calcination study showed that AgNO₃ precursor supported on alumina was decomposed under the beam to yield the same EXAFS spectra as for the calcined catalyst and further heating did not change EXAFS spectra and XRD patterns.

Study of the reducibility of Ag/Al₂O₃ showed higher reducibility of catalysts supposedly having lower Ag dispersion, i.e. bigger Ag_xO_y particles as suggested before using conventional TPR measurements. This is true for (probably, due to sintering of the precursor at high temperature). TPRs of Ag supported on pure or Si-doped alumina (both oxidized and reduced cases) also showed higher reducibility of the undoped sample (less active one) which can be related with bigger particles, i.e. worse Ag dispersion. Therefore, we have confirmed that a certain size of Ag_xO_y active sites is necessary for an active Ag/Al₂O₃ catalyst, however, the determination of the exact value still remains a challenge.

Acknowledgements

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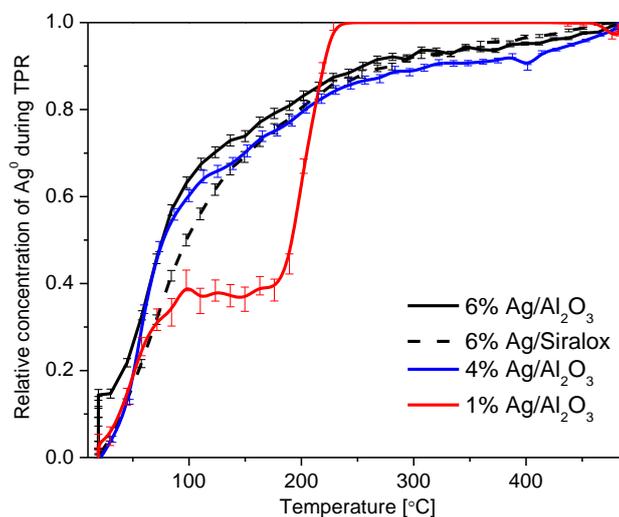


Fig. 3. Fraction of reduced Ag species determined by linear combination analysis of XANES spectra measured during temperature-programmed reduction of Ag/Al₂O₃.