

Deactivation of Vanadia-based SCR Catalysts by Phosphorus

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Introduction

Vanadia-based SCR catalysts may rapidly deactivate when fuels rich in phosphorus (e.g. sewage sludge, meat and bone meal, MBM) are combusted together with coal or oil at central power stations. Early studies on P-deactivation have assigned a relative weak poisoning strength to phosphorus [1, 2]. These studies, however, were all conducted by wet impregnation of the vanadia-based catalysts with aqueous solutions of phosphoric acid, H_3PO_4 , and the real mechanism of P deposition may produce a rather different scenario. The analysis of commercial monoliths exposed at full scale during MBM and sewage sludge co-firing has in fact shown a high accumulation of P in the catalyst walls [3], due to the formation of polyphosphates. Deactivation by polyphosphates can not be reproduced in the laboratory by the wet impregnation method normally employed during deactivation studies. These species can be formed at high temperatures by condensation reactions between the different P-acids or oxides present in the flue gas. They may be found at the inlet of the SCR reactor as aerosols, which will possibly deposit on the catalyst surface deactivating it. On the other hand, the analysis of catalysts employed at full-scale applications can not point out the influence of the polyphosphates on the total deactivation measured, due to the simultaneous presence of other deactivating species, especially alkali metals.

In the present work, commercial vanadia-based SCR full-length monoliths have been exposed in a pilot-scale setup to a flue gas from a natural gas burner to which H_3PO_4 was added.

Materials and Methods

The pilot-scale setup mainly consists of a 50 kW natural gas burner, a lance for injection of solutions in the flue gas, and a reactor hosting a monoliths $7.5 \times 7.5 \times 50 \text{ cm}^3$ in size. The catalysts employed were commercial Haldor Topsøe A/S DNX 3%wt $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$. The activity measurements have been performed at 350 °C, in the presence of 500 ppmv NO and 600 ppmv of NH_3 . Both the aerosol particle sizes and concentrations in the flue gas have been measured by a TSI SMPS. Three different monoliths have been exposed during addition of 10, 100 and 1000 ppmv of H_3PO_4 for 819, 38 and 24 hours respectively. Both the fresh and the spent catalysts have been characterized by Hg-porosimetry, SEM analysis and chemical composition. Moreover, the redox behaviour and state of V(IV) of the exposed catalysts have been analyzed by in situ electron paramagnetic resonance spectroscopy (EPR). The tests were conducted at 350 °C in the presence of 1000 ppmv NO, 1200 ppmv NH_3 , 5%v O_2 , 1%v H_2O and N_2 .

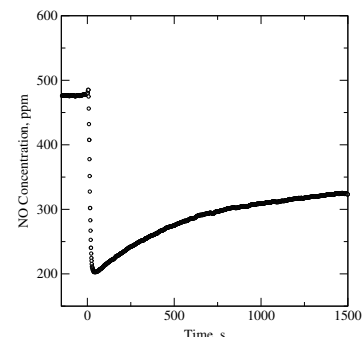


Figure 1. SCR activity measurement for the sample exposed to 100 ppm H_3PO_4 for 20 hours. NH_3 added from 0 s.

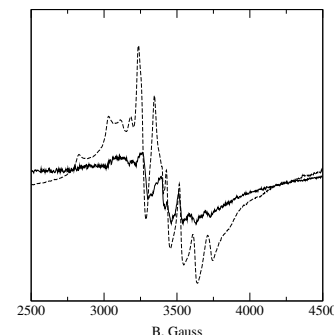


Figure 2. In situ EPR spectra for the catalysts exposed to 10 (—) and 100 ppm (---) H_3PO_4 . $T=350\text{ °C}$, SCR atmosphere.

Results and Discussion

SMPS measurements showed formation of polyphosphoric acid aerosols, with particle number concentrations in the order of $1 \cdot 10^{14} \text{ \#/m}^3$ at 350 °C and diameters $< 0.1 \text{ }\mu\text{m}$, indicating condensation of polyphosphoric acids from the gas phase. After the total exposure to 10, 100 and 1000 ppmv H_3PO_4 , the P-content measured within the catalyst at the outlet of the exposed samples was 3.0, 4.1 and 18.7 %wt. The activities of the monoliths were periodically measured during the whole exposure. The element exposed to 10 ppmv H_3PO_4 lost only 10% of its activity since the start of the addition, whereas the deactivation experienced by the monolith exposed to 100 ppmv of H_3PO_4 was much more severe. Around 58% of the original activity was in fact lost, even though the P-levels in the catalyst were not much higher than the sample exposed to only 10 ppm. In particular, during the activity measurements, the NO conversion showed a transient as a function of exposure to NH_3 (Figure 1). According to in situ EPR measurements (Figure 2), this transient was due to stabilization by P of the V(IV) groups, which are formed during the SCR reaction, and a subsequent decrease in redox properties.

Significance

The results obtained in this work [4] constitute the first reference about deactivation of vanadia-based catalysts explicitly due to polyphosphoric acid alone. It is believed they show the real deactivating potential of P, when this is present in the flue gas during post-treatment of combustion processes, which has been found much more poisonous than indicated by wet impregnated tests.

References

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