

Kinetic studies on the stability of Pt for NO oxidation: effect of sulfur

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Introduction

NO oxidation over Pt supported catalysts plays a key role in developing NOx abatement technologies for lean-burn engines. In previous work [1] we have studied the kinetics of the NO oxidation reaction over Pt/Al₂O₃ under differential conditions, accounting for product inhibition. Significant catalyst deactivation has been observed over a series of Pt catalyst over different supports and cluster sizes. We have correlated such deactivation with the oxidation state of the metal [2]. In conformity with these results we report here on the long term stability of Pt and the effect of adsorbed sulfur on the forward NO oxidation rate over a series of Pt/SBA-15 silica catalysts. In-situ X-ray Absorption Spectroscopy (XAS) experiments suggest that long term exposure (18h) to NOx increases the Pt-O coordination as compared to 1h of exposure. Surprisingly, we observe that reversible sulfur adsorption on Pt with the formation of Pt-O-SOx under NOx gas mixtures is accompanied by a 2-2.5 times increase in stable TORs relative to the rates for the un-sulfided catalysts at the same time on stream.

Materials and Methods

Three Pt/SBA-15 powder catalysts were used for this study with Pt particle sizes of 2, 4 and 9 nm. The kinetic measurements were done in a plug flow reactor under differential conversion using a typical exhaust composition of 300 ppm NO, 170 ppm NO₂, 10% O₂ at 1 atm total pressure and 3.5 L/min total flow rate. Activation energies and orders of reaction were determined by randomly changing the temperature and compositions over the following ranges: 250-300°C, 150-450 ppm NO, 120-400 ppm NO₂, 5-25% O₂. Samples were sulfided by first reducing them with H₂ at 250°C, followed by exposure to 380 ppm H₂S/25% H₂/N₂ and desorption of weakly adsorbed S with H₂ at 250°C. X-ray absorption measurements were made on the insertion-device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory.

Results and Discussion

Previous XAS time resolved experiments showed that the fraction of Pt²⁺ correlates well with the degree of deactivation observed for different particle sizes. Larger clusters are more resistant to oxidation and give a higher TOR. Such oxidation was seen to occur within 25 min under reaction conditions, after which the fraction of Pt²⁺ reached a steady level. Deactivation is also observed during our kinetic studies, with a drastic change during the first two hours and a slow variation occurring over much longer time periods. Recent findings suggest that long term exposure (18h) to NOx increases the Pt-O coordination as compared to 1h of exposure. These results may explain the long term decrease in activity observed in our kinetic measurements. Therefore, careful stabilization protocols were needed to compare rates

for different particle sizes. The stabilized rate for the 9 nm particle catalyst was 13 times higher than the TOR for the 2 nm one. It becomes clear that preventing Pt oxidation is the key step in improving catalyst performance for NO oxidation. In line with this argument we have also studied the effect of sulfur poisoning on different particle sizes of Pt on SBA-15. On the sulfided catalysts the initial rate of deactivation is smaller than for the corresponding un-sulfided samples. We have measured a 2-2.5 times increase in the stable TOR upon sulfidation for all three Pt cluster sizes, with the largest effect on the 9 nm particle (Fig 1a). We believe that sulfur withdraws electron density from Pt in such a way that the neighboring Pt atoms are now less likely to be oxidized. XAS experiments confirm the presence of Pt-S bonds on the 2 and 4 nm particles which completely become Pt-O after 1h of exposure to NOx. After re-reduction, Pt-S is observed again implying that under oxidation conditions Pt is not regenerated, but sulfur remains in the particle as Pt-O-SOx (Fig 1b). Even after long term exposure to NO oxidation conditions the EXAFS after reduction shows no decrease in Pt-S coordination. This is the first evidence of such behavior occurring on sulfur adsorption on Pt supported on a non S-adsorbing material such as SBA-15.

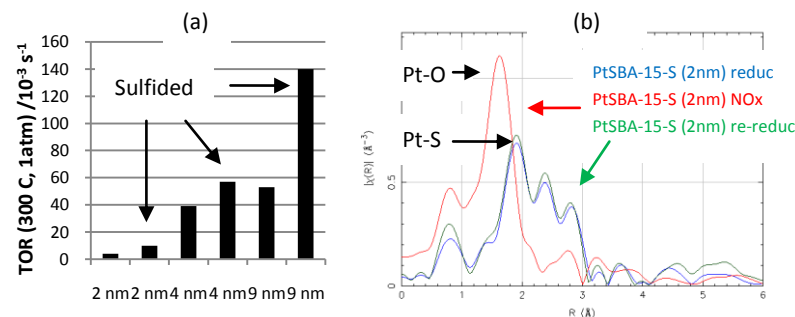


Figure 1. (a) Effect of pre-adsorbed sulfur on the rate of NO oxidation (300 ppm NO, 170 ppm NO₂, 10% O₂, bal N₂). (b) EXAFS evidence of reversible sulfur adsorption on pre-sulfided Pt.

Significance

Our kinetics studies confirm that the increase of Pt cluster size has a positive effect on the rate of NO oxidation. Such increase is caused by the intrinsic resistivity to oxidation as the particle grows in size. However, catalysts were seen to deactivate over long time periods as the Pt oxidizes. Upon sulfidation the rates of deactivation decrease leading to an increase in the stable TORs by a factor of 2-2.5, relative to the un-sulfided catalysts. Also, we have presented the first evidence that oxidation does not regenerate the catalyst, but rather sulfur stays in the Pt particle as a Pt-O-SOx species. Our results strongly suggest that preventing Pt oxidation is crucial in developing better catalysts for NO oxidation.

References

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