Supported platinum and palladium catalysts for passive SCR applications

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Abstract

Initial synthetic gas bench reactor tests (Fig 1, left panel) showed that NH₃ is formed over all catalyst formulations when the gas feed is net-reducing (S<1). For some Pt containing samples, the availability of very low oxygen concentration enhances NH₃ formation as compared to complete absence. For Pt/Al₂O₃ this effect is likely due to decreased self-poisoning by CO. This trend is also seen when hydrogen is directly available in the gas feed over TiO₂ supported catalysts due to the strong metal-support interaction properties of TiO₂. Transient experiments (Fig 1, centre panel) revealed commercial Pd/Al₂O₃ to be the most promising candidate for NH₃ formation thus far. The TWC also contained Pd and Al₂O₃ but its additional components (Rh, Ce) are thought to have inhibited the formation of NH₃ under cyclic conditions.

Introduction

In the present work we have investigated catalyst formulations that, under rich conditions, may enable on-board formation of NH₃ by using NO and hydrogen sources readily available in the exhaust stream. The formed NH₃ could be stored on a downstream SCR catalyst and used as a NOx reducer during lean operation. This method, termed selective passive catalytic reduction (passive-SCR), is presently investigated for gasoline fuelled vehicles operating under net-lean conditions and may result in a reduced dependence or even complete removal of the requirement for urea addition.

Materials and Methods

A series of six catalysts (platinum or palladium supported on either alumina, silica or titania) were prepared via incipient wetness impregnation and coated onto monoliths for use in a synthetic-gas-bench reactor. To determine whether hydrogen formed via the water-gas-shift (WGS) reaction is a viable option for NH₃ formation, and the effect that the presence of oxygen has on the gas. The formed NH₃ could store on a downstream SCR catalyst and used as a NOx reducer during lean operation. This method, termed selective passive catalytic reduction (passive-SCR), is presently investigated for gasoline fuelled vehicles operating under net-lean conditions and may result in a reduced dependence or even complete removal of the requirement for urea addition.

Results and Discussion

Initial synthetic gas bench reactor tests (Fig 1, left panel) showed that NH₃ is formed over all catalyst formulations when the gas feed is net-reducing (S<1). For some Pt containing samples, the availability of very low oxygen concentration enhances NH₃ formation as compared to complete absence. For Pt/Al₂O₃ this effect is likely due to decreased self-poisoning by CO. This trend is also seen when hydrogen is directly available in the gas feed over TiO₂ supported catalysts due to the strong metal-support interaction properties of TiO₂. Transient experiments (Fig 1, centre panel) revealed commercial Pd/Al₂O₃ to be the most promising candidate for NH₃ formation thus far. The TWC also contained Pd and Al₂O₃ but its additional components (Rh, Ce) are thought to have inhibited the formation of NH₃ under cyclic conditions.

In situ experiments are shown in Fig 1, right panel. In situ XAS experiments show that, as the gas feed becomes net-oxidizing, the intensity of the signal representing Pt-oxides increases rapidly and begins to level off when S=1.33. This structural trend is also observed in section (a) where the EXAFS spectra show an increase in Pt-O components, accompanied by a decrease in Pt-Pt components as the stoichiometric value of the gas feed increases. Section (b) shows that, as the gas feed tends towards lower stoichiometric values, the band corresponding to the NH stretch region increases in intensity over all samples. This is accompanied by a reduction in the contribution from gaseous CO and, inversely, an increase in the adsorption of CO. This implies that CO oxidation occurs as a side-reaction when oxygen is present in the feed, thus limiting the hydrogen that can be supplied via the WGS reaction. An additional route reported for NH₃ formation is the hydrolysis of surface cyanate groups. Though these groups are observed on Al₂O₃ supported samples under reducing conditions, they are suppressed in the presence of oxidizing feeds.

Significance

This investigation has shown that it is possible to form significant concentrations of NH₃ using water as a source of hydrogen although the effect of oxygen, under both steady-state and transient conditions, is one that must be addressed in future work if this is to be successfully implemented into a passive SCR application.

References