

# Bimetallic Ag-Based Catalysts for the Selective Catalytic Reduction of NO<sub>x</sub> Using Reformate and Propylene as Reductants

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## Introduction

Diesel engines offer significantly higher efficiencies than spark ignition engines; however, managing the emission of NO<sub>x</sub> and particulate matter presents unique challenges.<sup>1</sup> The selective catalytic reduction of NO<sub>x</sub> (SCR) has been used to convert NO<sub>x</sub> in oxygen-rich diesel exhaust streams to N<sub>2</sub>. A number of materials have been demonstrated to be active for this reaction including supported noble metals (e.g. Pt, Pd and Rh), supported precious metals (Ag and Au), and zeolites. However, these catalysts are not sufficiently active at temperatures below 300°C.<sup>2</sup>

The addition of small amounts of hydrogen to the exhaust has been shown to improve performance, in particular for Ag/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>3</sup> In principle, hydrogen would be produced by reforming hydrocarbons in the diesel or biodiesel fuel.<sup>4</sup> Notwithstanding the performance of Ag/Al<sub>2</sub>O<sub>3</sub> there is still a need for better performing catalysts. A detailed understanding of the mechanism for NO<sub>x</sub> SCR would facilitate development of new, better performing catalysts. The goals of research described in this paper are to evaluate the influence of promoters and co-catalysts on the performance of Ag-based catalysts, and explore the mechanism of SCR over these materials.

## Materials and Methods

A series of catalysts containing Pt, Pd or Rh, and Ag on three different supports (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub>) was prepared using the incipient wetness method. The metals were added via co-impregnation with aqueous metal salt solutions. The target loadings were 2 wt% for Ag and 0.5% for Pt, Pd or Rh. We focused on performance at temperatures between 200 and 400 °C, and atmospheric pressure. The feed composition consisted of 600 ppm NO, 800 ppm C<sub>3</sub>H<sub>6</sub>, 1600 ppm CO, 3200 ppm H<sub>2</sub>, 10% O<sub>2</sub>, 4% H<sub>2</sub>O, 8% CO<sub>2</sub>, and He as balance. A NO<sub>x</sub> analyzer was employed to measure the NO and NO<sub>2</sub> content. A Varian micro-GC was used to measure the amounts of CO, CO<sub>2</sub>, H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, N<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>O in the effluent.

## Results and Discussion

All of the Ag-based catalysts were active for NO<sub>x</sub> SCR. Unlike most of the catalysts which achieved a maximum NO<sub>x</sub> consumption rate at ~300 °C, rates for the Ag-Pt catalysts steadily increased, in particular for the Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> supported materials. This difference in the trends is likely due to differences in the active sites. NO<sub>x</sub> consumption rates are summarized in Figure 1, and the reductant conversions are summarized in Table 1. For the Ag-Pt/Al<sub>2</sub>O<sub>3</sub> and Ag-Pt/CeO<sub>2</sub> catalysts, all three reductants contributed to the reduction of NO<sub>x</sub> from 200-300 °C, but from 300-400 °C, C<sub>3</sub>H<sub>6</sub> was the only available reductant, as H<sub>2</sub> and CO were completely exhausted. For the TiO<sub>2</sub> supported catalyst, there was a slight increase in rate from 200-300 °C, largely due to the effect of C<sub>3</sub>H<sub>6</sub>, but from 300-400°C, H<sub>2</sub> and CO were

starved and C<sub>3</sub>H<sub>6</sub> was primarily burned. This suggests that for the Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> supported catalysts, H<sub>2</sub> assisted C<sub>3</sub>H<sub>6</sub> in the reduction below 300 °C and had no effect above this temperature. For the TiO<sub>2</sub> supported catalyst, the effect of H<sub>2</sub> was minimal below 300 °C, and most of the H<sub>2</sub> burned above 300 °C. From the few published studies where CO is co-injected with H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>, it has been reported as having an inhibiting effect,<sup>4</sup> although more research is required. In summary, major findings are that between 200-300 °C, the presence of H<sub>2</sub> appeared to enhance NO<sub>x</sub> SCR over Ag-Pt/Al<sub>2</sub>O<sub>3</sub> and Ag-Pt/CeO<sub>2</sub> but had minimal effect for Ag-Pt/TiO<sub>2</sub>, and that reformate is completely consumed by ~300 °C.

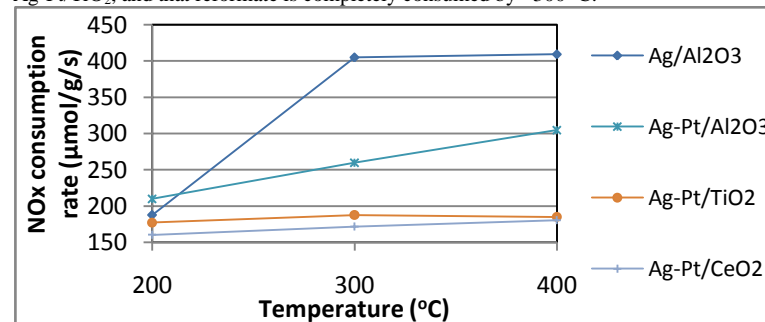


Figure 1: NO<sub>x</sub> consumption rates for Ag-Pt-based catalysts- (600 ppm NO, 800 ppm C<sub>3</sub>H<sub>6</sub>, 1600 ppm CO, 3200 ppm H<sub>2</sub>, 10% O<sub>2</sub>, 4% H<sub>2</sub>O, 8% CO<sub>2</sub>, balance He, GHSV = 60000 1/hr).

Table 1: Total reductant conversion for Ag-Pt-based catalysts (conditions same as in Fig. 1).

Temperature	Ag/Al <sub>2</sub> O <sub>3</sub>	Ag-Pt/Al <sub>2</sub> O <sub>3</sub>	Ag-Pt/TiO <sub>2</sub>	Ag-Pt/CeO <sub>2</sub>
200	30	69	30	42
300	64	85	60	89
400	82	92	95	95

## Significance

New EPA standards for NO<sub>x</sub> emissions that are scheduled to go into effect in 2010 for on-road vehicles and 2015 for off-road vehicles will require a 90% reduction in emitted NO<sub>x</sub> compared to 2005 levels.<sup>5</sup> Achieving these standards will require new after-treatment systems for diesel exhaust. NO<sub>x</sub> SCR with hydrocarbons and H<sub>2</sub> has shown promise, especially if the reformate can be produced on-board the vehicle so that a single tank is required.

## References

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