NOx Reduction and NH\textsubscript{3} Production over Silver-Alumina Catalysts with Oxygenated Hydrocarbons

Josh A. Pihl\textsuperscript{1}, Galen B. Fisher\textsuperscript{2}, William L. Johnson\textsuperscript{1} and Todd J. Toops\textsuperscript{3,4}

\textsuperscript{1}Oak Ridge National Laboratory, Oak Ridge, 37831 U.S.A.
\textsuperscript{2}University of Michigan, Ann Arbor, Michigan 48109-2136 U.S.A.
\textsuperscript{3}toopstj@ornl.gov

Introduction

Supported Ag on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} has been shown to be an effective catalyst for selectively reducing NO\textsubscript{x} to N\textsubscript{2} in a wide temperature range with various hydrocarbons and oxygenates typically found in fuels used in mobile systems. Additionally, this reactivity has been demonstrated at a range of hydrocarbon to NO\textsubscript{x} (HC/NO\textsubscript{x}) ratios that would not introduce a severe fuel penalty\cite{1}. A particularly effective HC for this selective catalytic reduction (SCR) of NO\textsubscript{x} is ethanol, which is found at low levels in all gasoline and is becoming more prevalent in concentration and availability in domestic automotive fuels (e.g., E85). Fisher et al.\cite{2,3} have demonstrated that flowing NO\textsubscript{x} and ethanol vapor (and other HCs) over these same Ag-based catalysts can form NH\textsubscript{3} under lean conditions, which can then be used with a downstream zeolite-based NH\textsubscript{3}-SCR catalyst to produce NO\textsub{x} conversions in excess of 90\% for realistic exhaust streams in lean burn engine systems. This important finding may offer an alternative to urea dosing currently being implemented with several NH\textsubscript{3}-based SCR systems using either zeolite- or vanadia-based catalysts\cite{4}. All of these recent findings point to the importance of studying this chemistry and determining the important factors in ammonia formation. Using DRIFTS along with reactor studies we are able to describe this chemistry in more detail and report the first results that correlate the formation of ammonia with ethanol concentration under lean NO\textsubscript{x} conditions.

Materials and Methods

A 2 wt.% Ag/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} catalyst was synthesized using the incipient wetness technique with a AgNO\textsubscript{3} precursor. Additionally, a washcoated commercial Ag/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} was obtained from Catalytic Solutions. Catalysts were calcined at 700 °C for 15 h in flowing air and evaluated at gas hourly space velocities (GHSV) ranging from 30k to 180k h\textsuperscript{-1} in temperatures from 200 to 550 °C. Feed gas conditions were 500 ppm NO, 10% O\textsubscript{2}, 5% H\textsubscript{2}O, with variable amounts of ethanol (250-2000 ppm) at 30k h\textsuperscript{-1} GHSV (balance Ar). All gas flows were controlled by mass flow controllers with H\textsubscript{2}O and ethanol introduction using impingers submersed in temperature controlled baths. Chemiluminescent NO\textsubscript{X} analyzers were used in conjunction with a quadrupole mass spectrometer for gas-species analysis.

Results and Discussion

In Figure 1 the product distribution for ethanol SCR of NO\textsubscript{x} under lean conditions is shown for the temperature window of 200-550 °C with Ag/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} at 30k h\textsuperscript{-1} GHSV. At 30k h\textsuperscript{-1} and a HC/NO\textsubscript{x}=3 we see clear evidence of three regions of correlated products being formed for N- and C-containing species up to 450°C in the following order:

\[
\text{EtOH} + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{NO}_2 \rightarrow [\text{CO}_2 + \text{CO}] + [\text{N}_2 + \text{NH}_3]
\]

Ethanol and NO react in the presence of oxygen starting at 200 °C to form acetaldehyde and NO\textsubscript{2}. Between 275 and 450°C, ethanol and NO form CO\textsubscript{2}, CO, N\textsubscript{2}, and NH\textsubscript{3}. Above 450 °C, behavior depends on HC/NO\textsubscript{x} ratio. As we have discussed recently\cite{5}, the NO\textsubscript{2} and acetaldehyde release correlates with the decrease in adsorbed nitrate and acetate monitored by DRIFTS. At higher temperatures CO\textsubscript{2}, CO, N\textsubscript{2}, and NH\textsubscript{3} are all formed via much less stable intermediates. In Figure 2 the selectivity to NH\textsubscript{3} (versus N\textsubscript{2}) increases greatly as the HC/NO\textsubscript{x} ratio increases from 1 to 8, reaching more than 40% at 350 °C for a HC/NO\textsubscript{x} ratio of 8.

Additional efforts are being made to investigate the ability of ethanol and butanol to promote the NO\textsubscript{x} removal activity of hydrocarbons that would be found in gasoline exhaust, similar to the way H\textsubscript{2} has been shown to promote low temperature NO\textsubscript{x} removal with hydrocarbons.

Materials and Methods

A 2 wt.% Ag/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} catalyst was synthesized using the incipient wetness technique with a AgNO\textsubscript{3} precursor. Additionally, a washcoated commercial Ag/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} was obtained from Catalytic Solutions. Catalysts were calcined at 700 °C for 15 h in flowing air and evaluated at gas hourly space velocities (GHSV) ranging from 30k to 180k h\textsuperscript{-1} in temperatures from 200 to 550 °C. Feed gas conditions were 500 ppm NO, 10% O\textsubscript{2}, 5% H\textsubscript{2}O, 750 ppm ethanol at 30k h\textsuperscript{-1}. (b) NH\textsubscript{3} formation as a function of ethanol concentration for HC/NO\textsubscript{x} ratios of 1, 3, and 8 under lean NO\textsubscript{x} SCR conditions, reaching >40% selectivity to NH\textsubscript{3} at 350 °C with 2000 ppm of ethanol.

Significance

Several factors suggest that ethanol, and/or butanol, will rise in importance as transportation fuels. Understanding their ability to provide a potential non-urea pathway to NO\textsubscript{x} reduction with alcohol-based fuels may facilitate the implementation of a non-precious metal emissions control system that is applicable in lean burn vehicles.

References