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Selective catalytic reduction of nitric oxide with ethanol/gasoline blends over a silver/alumina catalyst

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ABSTRACT

Lean gasoline engines running on ethanol/gasoline blends and equipped with a silver/alumina catalyst for selective catalytic reduction (SCR) of NO by ethanol provide a pathway to reduced petroleum consumption through both increased biofuel utilization and improved engine efficiency relative to the current stoichiometric gasoline engines that dominate the U.S. light duty vehicle fleet. A pre-commercial silver/alumina catalyst demonstrated high NO_x conversions over a moderate temperature window with both neat ethanol and ethanol/gasoline blends containing at least 50% ethanol. Selectivity to NH_3 increases with HC dosing and ethanol content in gasoline blends, but appears to "saturate" at around 45%. NO_2 and acetaldehyde behave like intermediates in the ethanol SCR of NO. NH_3 SCR of NO_x does not appear to play a major role in the ethanol SCR reaction mechanism. Ethanol is responsible for the low temperature SCR activity observed with the ethanol/gasoline blends. The gasoline HCs do not deactivate the ethanol SCR activity, but they also do not appear to be significantly activated by the presence of ethanol.

1. Introduction

Concerns about greenhouse gas emissions and dependence on foreign petroleum supplies have motivated governments around the world to develop regulations that require significant improvements in vehicle fuel economy and/or substantial increases in biofuel utilization in the coming years. These regulations have inspired vehicle manufacturers to pursue a range of technologies that reduce petroleum consumption. To ensure their adoption in the marketplace, these technologies must comply with increasingly stringent exhaust emissions regulations for pollutants such as nitrogen oxides (NO_x), carbon monoxide, and hydrocarbons (HCs).

In the U.S., the light duty vehicle fleet is dominated by internal combustion engines fueled with gasoline [1]. These engines operate with a stoichiometric mixture of fuel and air to enable emissions control with three-way catalyst (TWC) technology. Lean operation (with excess air) could boost gasoline engine efficiency by 10–20% over comparable stoichiometric engines [2]. While TWCs effectively oxidize CO and HCs under lean conditions, they are unable to reduce NO_x in the presence of excess oxygen. Thus, controlling NO_x in a cost-effective and fuel-efficient manner is a critical barrier to deploying lean gasoline engines, which could significantly reduce the petroleum consumption of the U.S. light duty vehicle fleet.

In addition to fuel economy regulations, the U.S. government has implemented mandates for biofuel consumption aimed at reducing petroleum dependence [3]. Nearly all gasoline in the U.S. is blended with 10% ethanol, and E85 (gasoline blended with 51–83% ethanol) is available at many fuel stations. The adoption of E85 by U.S. consumers has been limited by the lower volumetric energy content of ethanol, which results in lower tank mileage and higher operating costs. Ethanol, however, presents other advantages that have not yet been fully exploited. Previous studies have shown that ethanol is a very effective reductant for the selective catalytic reduction (SCR) of NO over Ag/Al_2O_3 catalysts in lean exhaust environments [4–22]. In fact, other non-alcohol HC reductants can only achieve low temperature NO_x reduction activity comparable to alcohols through addition of H_2 to the exhaust stream to promote the HC SCR reactions [5–8,20]. Another potential advantage of ethanol is its relatively high yield of NH_3 during the SCR of NO_x over Ag/Al_2O_3. The ability to generate NH_3 under lean operating conditions creates possibilities for the application of commercially proven zeolite-based NH_3 SCR catalysts without the additional complexity and cost of urea storage and delivery. This would be accomplished through HC SCR/NH_3 SCR dual catalyst system architectures such as the ones tested by Fisher et al. [5] (single cylinder engine), DiMaggio et al. [6] (flow reactor), and others, including Nam et al. [9].

Through its high NO_x conversion activity or NH_3 production capacity, ethanol SCR of NO over Ag/Al_2O_3 has the potential to

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control the NO_x emissions from lean gasoline engines without the need for onboard urea storage or prohibitively expensive catalysts with high precious metal loadings. Thus, the widespread availability of alcohol-based biofuels in the U.S. presents an opportunity to both increase engine efficiency and boost biofuel utilization through lean burn gasoline engines equipped with Ag/Al_2O_3 SCR catalysts.

The specific goals of this work were to evaluate the feasibility of using ethanol/gasoline blends for SCR of NO over a commercially relevant Ag/Al_2O_3 catalyst, to identify appropriate operating regimes and performance limitations, and to clarify the catalytic reaction chemistry to identify the underlying causes of performance limitations. This effort builds on earlier work [16] that identified key mechanistic attributes of the system, including: the rapid dehydrogenation of ethanol to form acetaldehyde and adsorbed acetates; the persistence of acetates to fairly high temperatures; the ethanol promotion of NO oxidation to NO_2 and formation of adsorbed nitrates; and the disappearance of nitrates upon nitrogen production. Furthermore, the NH_3 generation strategy introduced recently [5,6] was explored in the context of ethanol/gasoline blends.

2. Material and methods

2.1. Catalyst sample

The catalyst used in all of the experiments described here was a 2 wt% Ag/Al_2O_3 provided by Catalytic Solutions, Inc. (now a part of Clean Diesel Technologies, Inc.). The catalyst was washcoated on a 62 cells/cm^2 cordierite monolith by the supplier. A 2 cm diameter 5 cm long core was cut from the face of the monolith brick and loaded into an automated flow reactor. Prior to any experiments, the core sample was degreened for 3 h at 600 °C under 10% O_2, 5% H_2O, balance N_2 at a gas hourly space velocity (GHSV) of 35,000 hr^{-1} to ensure stable operation during subsequent evaluation.

2.2. Automated flow reactor

All experiments were conducted on an automated flow reactor that uses synthetic exhaust gas mixtures to evaluate catalyst performance, properties, and chemistry. Metal-sealed mass flow controllers (MKS Instruments) were used to meter the flow of gaseous species from compressed gas (or cryogenic liquid) cylinders (Air Liquide Americas) to generate gas mixtures with the desired composition. Water was introduced through a custom vapor delivery system consisting of: an HPLC pump (Eldex Laboratories); a liquid preheater made from a 1.6 mm outer diameter (OD) 1 m long stainless steel tube wrapped around a 9.5 mm diameter cartridge heater; and a stainless steel capillary (1.6 mm OD, 0.18 mm ID, 100 mm long) that injected the water vapor into a 200 °C inert gas stream. Liquid hydrocarbons were metered with a syringe pump (Chemyx) and delivered through a stainless steel capillary (1.6 mm OD, .13 mm ID, 100 mm long) into the preheated gas stream. All of the reactor gas lines (6.4 mm OD) were heated to roughly 200 °C to prevent condensation or adsorption of reacting species.

The catalyst core sample was wrapped in fiberglass strands (previously calcined in air to 650 °C) and loaded in a 2.5 cm OD quartz tube. The upstream portion of the quartz tube was filled with 3 mm quartz chips to increase heat transfer to the inlet gas stream and improve temperature uniformity. The quartz tube was fitted with graphite ferrules and custom stainless steel end caps that connected to the reactor gas lines and provided inlet ports for thermocouples and pressure transducers. The quartz tube assembly was placed in a tube furnace (Lindberg Blue/M) to precisely control the catalyst temperature. Type K thermocouples (0.5 mm diameter) were deployed 5 mm upstream, 5 mm downstream, and at the midpoint inside the catalyst core sample to monitor catalyst temperatures. Reactor pressures were monitored with silicon-diaphragm absolute pressure transducers (Omegadyne). Inlet and outlet gas compositions were measured with a Multigas 2030HS FTIR spectrometer (MKS Instruments). A custom LabVIEW (National Instruments) interface provided automated data acquisition and system control.

Table 1
EEE-Lube Cert Gasoline properties.

Property	Unit	Value
C	wt%	86.5
H	wt%	13.5
O	wt%	<0.01
S	ppmw	4
Aromatics	vol%	27.9
Olefins	vol%	1.0
Saturates	vol%	71.7
RON	–	97.0
MON	–	88.1

2.3. Fuel mixtures

The potential fuel compositions that a HC SCR catalyst could encounter in a real-world lean gasoline application vary widely. For example, the "E85" available at fueling stations can range in composition between 51% and 83% ethanol by volume [23]. Standard gasoline typically contains 10% ethanol by volume, but it can contain up to 15%. A flex-fuel vehicle that can run on either gasoline or "E85" could conceivably end up with a fuel tank composition ranging anywhere from 10 to 83% ethanol after partial tank fills. To capture this range of fuel compositions and to explore the role of the fuel components in the HC SCR of NO_x, we used a wide range of fuel compositions blended from two feedstocks: 200 proof ethanol (Decon Laboratories) and EEE-Lube Certification Gasoline (Haltermann Solutions). The blends were created by measuring appropriate volumes of each component and mixing them by shaking in a 1 l metal can. The properties of the gasoline are listed in Table 1. Note that the gasoline contained a representative level of aromatics as well as a low level of sulfur, but no ethanol. The compositions of the fuel blends used in this study are shown in Table 2.

2.4. Experiment protocols

All experiments discussed below were conducted at a GHSV of 35,000 h^{-1} (based on total monolith volume and flows at standard temperature and pressure). Feed gas mixtures always included 10% O_2 and 5% H_2O and used N_2 as the balance gas. Prior to each experimental run, the catalyst was pretreated in an attempt to remove HCs, coke, or sulfur species adsorbed during the prior experiment. This pretreatment was performed at a catalyst temperature of 600 °C and consisted of 2 steps: 10 min under 1% H_2 and 5% H_2O followed by 10 min under 10% O_2 and 5% H_2O. After the pretreatment,

Table 2
Composition of ethanol/gasoline blends.

Blend	Ethanol (%, v/v)	Gasoline (%, v/v)
E100	100	0
E85	85	15
E50	50	50
E15	15	85
E0	0	100