The Selective Catalytic Reduction of NO_x Over Ag/Al₂O₃ with Isobutanol as the Reductant

D. William Brookshear^{*}, Josh A. Pihl, Todd J. Toops, Brian West, Vitaly Prikhodko

Oak Ridge National Laboratory, Oak Ridge, TN 37831 United States

^{*}Corresponding Author: Daniel W. Brookshear

brooksheardw@ornl.gov

1-865-946-1242

2360 Cherahala Blvd, Knoxville, TN 37932

Abstract

This study investigates the potential of isobutanol (iBuOH) as a reductant for the selective catalytic reduction (SCR) of NO_x over 2 wt% Ag/Al₂O₃ between 150 and 550°C and gas hourly space velocities (GHSV) between 10,000 and 35,000 h⁻¹. The feed gas consists of 500 ppm NO, 5% H₂O, 10% O₂, and 375-1500 ppm iBuOH (C₁:N ratios of 3-12); additionally, blends of 24 and 48% v/v iBuOH in gasoline are evaluated. Over 90% NO_x conversion is achieved between 300 and 400°C using pure iBuOH, including a 40% peak selectivity towards NH₃ that could be utilized in a dual HC/NH₃-SCR configuration. The iBuOH/gasoline blends are only able to achieve greater than 90% NO_x conversion when operated at a GHSV of 10,000 h⁻¹ and employing a C₁:N ratio of 12. Iso-butyraldehyde and NO₂ appear to function as intermediates in the iBuOH-SCR mechanism, which mirrors the mechanism observed for EtOH-SCR. In general, the performance of iBuOH in the SCR of NO_x over a Ag/Al₂O₃ catalyst is comparable with that of EtOH, although EtOH/gasoline blends display higher NO_x reduction than iBuOH/gasoline blends. The key parameter in employing alcohols in SCR appears to be the C-OH:N ratio rather than the C₁: N ratio.

Keywords: isobutanol; hydrocarbon SCR; Ag/Al₂O₃

1. Introduction

The majority of light-duty vehicles in the United States utilize gasoline-powered internal combustion engines which operate under stoichiometric conditions, enabling the use of three-way catalyst (TWC) to meet emissions control standards [1]. However, it has been shown that operating these engines under lean conditions with excess air can boost engine efficiency by as much as 10-20% [2]. This presents an emissions control challenge as TWCs are not capable of reducing nitrogen oxides (NO_x) in an

environment with excess oxygen. Therefore, an alternative strategy for NO_x abatement is necessary, and must be both cost effective and fuel efficient in order to avoid negating the engine efficiency benefit gained by lean operation of gasoline engines.

One potential approach to addressing this issue is the selective catalytic reduction (SCR) of NO_x using fuel-derived reductants over Ag/Al₂O₃ catalysts. Previous studies have shown that these catalysts are more active for the SCR of NO_x using alcohol, as other organic gas reductants exhibit limited NO_x abatement without the addition of H₂ in the exhaust stream [3- 8]. In particular, ethanol (EtOH) has been heavily investigated as a hydrocarbon (HC) reductant for NO_x over Ag/Al₂O₃ due to its prevalence in commercially available gasoline in the United States and its promising NO_x reduction activity [3-22]. Recently, there has been interest in the feasibility of isobutanol (iBuOH) as an alternative bio-derived fuel which can readily be blended with gasoline and has some advantages over ethanol. Due to its higher energy density, iBuOH provides better fuel economy than EtOH on a volumetric basis, and its lower oxygen content allows it to be blended into gasoline at higher levels while still being compatible with existing vehicles [23]. Further, under the Renewable Fuel Standard (RFS) created in 2005, which was later expanded by the Energy Independence and Security Act (EISA) of 2007, a certain amount of biofuel must be blended into transportation fuel each year [24]. The Environmental Protection Agency (EPA) regulates this by assigning Renewable Identification Numbers to each gallon of biofuel produced and requiring companies which produce or blend fuels to meet an annual RINs quota [25]. Due to its higher energy density, isobutanol has the potential to generate more RINs than EtOH, thus making it easier for iBuOH producers to meet the RINs requirement. Processing plants which produce EtOH can readily be converted to iBuOH production, making it an attractive alternative biofuel.

Recent research on iBuOH has focused on its impact on engine performance and emissions from gasoline engines. It has been shown that iBuOH can be blended into gasoline at levels up to 50% by

volume (iBu50) with little to no modifications to the engine system required for successful operation [23, 26-29]. However, despite the drop-in viability of iBuOH and its potential benefits relative to EtOH, little research has been done to evaluate the viability of iBuOH-SCR of NO_x over Ag/Al₂O₃. Other butanol isomers have shown promising results as HC reductants, but with companies such as Gevo and Butamax focused on iBuOH production, it is desirable to determine its capability in this context [8, 12, 30].

Current Tier 2 Bin 5 emissions standards, which will remain in effect until 2017, require less than 70 mg/mi of NO_x exiting the tailpipe of light-duty vehicles for a full useful life of 120,000 miles. Tier 3 emissions standards will come into effect in 2017, and combine NO_x with non-methane organic gases (NMOG) into a single requirement along with increasing the full useful life requirement to 150,000 miles for light-duty vehicles [31]. In 2017 total NMOG + NO_x emissions must be below 86 mg/mi, and by 2025 light-duty vehicles will be limited to total NMOG + NO_x emissions of 30 mg/mi for the useful life of the vehicle. Thus, due to the increasingly stringent emissions standards in place, a viable emissions control system must convert the vast majority of both NO_x and NMOG in the exhaust. While the aftertreatment system performance requirements will be determined by application-specific engine exhaust characteristics, for the purposes of this study, it is assumed that a minimum of 90% of the NO_x exiting the engine must be reduced by the SCR catalyst for this strategy to even be considered for use on lean-burn gasoline engines.

The goal of this project is to assess the feasibility of using iBuOH and iBuOH/gasoline blends for the SCR of NO_x over a 2 wt% Ag/Al₂O₃ catalyst provided by a commercial supplier. The optimal operating conditions will be determined, and the performance of iBuOH as a HC reductant will be compared against that of EtOH. Additionally, some discussion of the mechanism for iBuOH-SCR over Ag/Al₂O₃ is included. This research expands on earlier efforts focused on EtOH-SCR which worked to identify the

operating regimes for maximum NO_x conversion with EtOH as the reductant, and discussed the SCR mechanism for EtOH over Ag/Al₂O₃ [9, 18].

2. Materials and methods

2.1 Ag/Al₂O₃ catalyst

The catalyst used in the current investigation was provided by Clean Diesel Technologies, Inc. (formerly Catalytic Solutions, Inc.) and consists of 2 wt% Ag/Al₂O₃ washcoated onto a cordierite monolith with a cell density of 62 cells/cm². Experiments are conducted on a core sample 2 cm in diameter and 5 cm in length cut from the face of the monolith. Prior to SCR evaluation, the catalyst is degreened at 600 °C for 3 h at a gas hourly space velocity (GHSV) of 35,000 h⁻¹ with a flow consisting of 5% H₂O, 10% O₂, and N₂ balance.

2.2 Automated flow reactor

Reactivity of the Ag/Al₂O₃ catalyst is measured on an automated flow reactor which simulates automotive exhaust compositions and temperatures. Gaseous species are introduced into the system from compressed gas cylinders via MKS Instruments mass flow controllers which meter the flows in order to achieve the desired simulated exhaust gas mixture. An Eldex Laboratories HPLC pump introduces liquid water through a custom designed water vapor delivery system, which consists of a 1 m stainless steel tube with a 1.6 mm outer diameter (OD) wrapped in a coil around a 9.5 mm diameter cartridge heater. After passing through the stainless steel coil, the water vapor is injected into a 200 °C inert gas stream (N₂) through a 100 mm stainless steel capillary with a 1.6 mm OD and 0.18 mm inner diameter (ID). Liquid iBuOH and iBuOH/gasoline blends are injected with a Chemyx syringe pump into the preheated gas stream through a separate stainless steel capillary with identical dimensions. The

stainless steel gas lines in the flow reactor have an OD of 6.4 mm and are heated to approximately 200 °C in order to avoid condensation or adsorption of reacting gases.

The Ag/Al₂O₃ catalyst core is loaded into a quartz tube and placed into a Lindberg Blue M Mini Mite furnace which controls reaction temperature. Smaller quartz tubes 23 cm in length with a 3 mm OD and 1 mm ID are loaded into the large quartz tube upstream of the catalyst sample to ensure adequate heat transfer to the simulated exhaust gases and to provide a more uniform temperature. Specially built stainless steel end caps connect either end of the large quartz tube to the stainless steel gas lines of the reactor. Ports in the stainless steel end caps allow inlets for thermocouples and pressure transducers. Omega Type K thermocouples are located 5 mm from the core inlet, 5 mm from the core exit, and at the midpoint of the catalyst core to record the temperature profile across the catalyst during experiments. Omegadyne silicon diaphragm absolute pressure transducers monitor the reactor pressure upstream and downstream of the catalyst sample. The composition of the simulated exhaust gas is measured at the inlet and exit of the catalyst core using an MKS Multigas 2030HS FTIR Spectrometer. Data acquisition and flow reactor control are accomplished with a custom LabVIEW interface which allows the operator to program the system for automated operation during experiments.

2.3 Experimental protocol

All SCR performance evaluations use simulated exhaust mixtures containing 5% H₂O, 10% O₂, 500 ppm NO, and N₂ balance. Unless otherwise specified, the GHSV is 35,000 h⁻¹. The catalyst is evaluated over a broad temperature range: 150-325 °C at 25 °C increments and 350-550 °C at 50 °C increments. In order to ensure steady state is reached, the catalyst is maintained at each temperature for approximately 25 minutes. The initial series of experiments examined the SCR activity of pure iBuOH at different reductant doses based on the carbon to nitrogen (C₁:N) ratio as determined by the concentrations of iBuOH and NO at the catalyst inlet. For example, a C₁:N ratio of 9 would correspond to 1125 ppm iBuOH and 500

ppm NO since iBuOH contains four carbon atoms. Pure iBuOH SCR performance is evaluated with $C_1:N$ ratios between 3 and 12, with the flow compositions shown in Table 1.

In addition to pure iBuOH, iBuOH/gasoline blends are also evaluated for SCR performance since the focus of the project is on lean gasoline applications. The gasoline used in the current study for fuel blending is EEE Lube Certification Gasoline provided by Haltermann Solutions. The detailed composition of this gasoline, based on the certificate of analysis, is shown in Table 2. Two different iBuOH blend levels were tested: 24 and 48 %v/v (iBu24 and iBu48, respectively). An iBuOH blend level of 24% is chosen due to the fact that it has the same oxygen content as E15 and thus is expected to be the maximum blend limit for iBuOH, while the 48% blend level provides a basis for comparison against higher EtOH blend levels as would be found in commercially available “E85”. $C_1:N$ ratios for the blends are calculated based on the carbon content of both the iBuOH and the gasoline components. The gasoline carbon content is calculated from the carbon weight fraction (Table 2) and the density of the gasoline (0.742 g/mL, provided in the certificate of analysis). These numbers are used to calculate the molar content of carbon per mL of gasoline, and this is utilized along with the blend level of iBuOH in gasoline and the molar content of carbon in isobutanol to determine overall $C_1:N$ ratio for an experiment. Both iBu24 and iBu 48 blends are evaluated at $C_1:N$ ratios of 6, 12, and 18 [23].

3. Results and Discussion

3.1 Pure iBuOH for SCR of NO

3.1.1 iBuOH: NO_x conversion

NO_x conversion over Ag/Al₂O₃ using pure iBuOH as the reductant is shown for a wide range of $C_1:N$ ratios in Figure 1. At $C_1:N$ ratios of 4.5 or less, NO_x conversion peaks at 85% or less, with the maximum conversion in a narrow temperature window centered around 325 °C. Higher $C_1:N$ ratios yield increased

NO_x conversions over wider operating windows. At C₁:N = 6 NO_x conversion increases to greater than 90% at temperatures between 300 and 350 °C, while increasing the C₁:N to 9 or above extends this peak conversion temperature window to 400 °C. In vehicle applications, tuning HC dosing to provide optimal SCR performance with the minimum required iBuOH will be a key factor determining the viability of this approach, as any iBuOH introduced into the exhaust system for SCR results in a fuel penalty that reduces the efficiency benefit of lean gasoline operation. If an exhaust mixture is assumed to consist of 500 ppm NO and 5% CO₂, a C₁:N ratio of 6 would require injection of an extra 3000 ppm (or 0.3%) C in the exhaust. Compared to the 5% CO₂ that results from burning fuel in the engine, this iBuOH dose would constitute a fuel penalty of roughly 0.3%/5.0% = 0.06 or 6% of the fuel fed to the engine. From a greenhouse gas perspective, an iBuOH dose at a C₁:N ratio of 6 would generate an extra 3000 ppm CO₂, which would increase the CO₂ exhaust concentration from 5% to 5.3%.

3.1.2 iBuOH: reductant conversion

Tracking all of the carbon species exiting the catalyst during iBuOH-SCR is challenging due to the complex partial oxidation chemistry that can occur over the Ag catalyst and the limited number of HC methods available on the FTIR software. However, it is useful to examine the more abundant species measured at the catalyst exit as a way to monitor conversion of the iBuOH reductant. Yields for CO, CO₂, butyraldehyde (C₃H₇CHO), and the remaining organic species are shown in Figure 2 for C₁:N ratios between 3 and 12, and are calculated based on total reactive carbon input according to equations R1-R4.

$$y_{CO} = \frac{C_{CO}}{C_{C,in}} \quad (R1)$$

$$y_{CO_2} = \frac{C_{CO_2}}{C_{C,in}} \quad (R2)$$

$$y_{C_3H_7CHO} = \frac{C_{C_3H_7CHO}}{C_{C,in}} \quad (R3)$$

$$y_{C,other} = 1 - y_{CO} - y_{CO_2} - y_{C_3H_7CHO} \quad (R4)$$

Below 250 °C, a significant amount of butyraldehyde is measured at the exit of the catalyst, peaking between 175 and 250 °C depending on C₁:N ratio. At these low temperatures, the bulk of the C fed to the catalyst exits as other organic species, including methane, ethylene, and propane. The yield of butyraldehyde decreases as the catalyst becomes more active for SCR and disappears by 350 °C. It is likely this compound is actually iso-butyraldehyde, corresponding to partial oxidation of the isobutanol reductant, but an iso-butyraldehyde FTIR quantification method was not available during this research. However, the observed behavior for butyraldehyde (appearance at low temperatures, disappearance coinciding with onset of NO_x reduction) suggests that partial oxidation of the isobutanol to iso-butyraldehyde or related surface adsorbates is an intermediate step in the NO SCR process. Above 350 °C, the majority of the carbon is exiting the catalyst as CO₂, with around 10% selectivity towards CO. At this higher temperature range, the isobutanol reductant is being directly oxidized to CO and CO₂, and the corresponding drop in reductant availability for SCR can be observed in the NO_x conversion curves of Figure 1.

3.1.3 Nitrogen speciation during iBuOH-SCR of NO

Detailed speciation of the N-containing products exiting the catalyst can yield valuable insights into the chemical reactions underlying the SCR of NO. Figure 3 plots the yield of each nitrogen species exiting the catalyst calculated according to equations R5-R9 based on the total reactive nitrogen species introduced at the inlet (500 ppm NO).

$$y_{NO} = \frac{C_{NO}}{C_{N,in}} \quad (R5)$$

$$y_{NO_2} = \frac{C_{NO_2}}{C_{N,in}} \quad (R6)$$

$$y_{NH_3} = \frac{C_{NH_3}}{C_{N,in}} \quad (R7)$$

$$y_{N_2O} = \frac{C_{N_2O}}{C_{N,in}} \quad (R8)$$

$$y_{N_2} = 1 - y_{NO} - y_{NO_2} - y_{NH_3} - y_{N_2O} \quad (R9)$$

From the trends observed in these plots, the activity over the catalyst can be separated into three distinct regions on the basis of temperature.

At temperatures below 250 °C, the primary activity over the catalyst is the oxidation of NO to NO₂, along with a small amount of N₂O formation. Peak NO₂ production occurs at 225 °C with a yield of 0.3, regardless of C₁:N ratio. It has been shown that this catalyst does not oxidize NO with a flow consisting of only O₂ and H₂O as the other constituents, and thus iBuOH, or some other reductant, is required for NO₂ formation [9]. N₂O production reaches a maximum at 225 or 250 °C, depending on C₁:N ratio, but never exceeds a yield of 0.08.

The temperature window from 250-450 °C is where iBuOH is most active as a reductant for the SCR of NO_x over Ag/Al₂O₃, although trends for the nitrogen species in this temperature range are highly dependent on C₁:N ratio. NO₂ yield is significant at C₁:N ratios less than 6, but decreases to near zero as the C₁:N ratio increases. The formation of NO₂ at low temperatures and disappearance at higher temperatures suggests that NO oxidation is likely an intermediate step in the mechanism for NO SCR by iBuOH over this catalyst. N₂O production in this temperature range remains small, and decreases as the temperature rises for all C₁:N ratios. The N₂ yield plot displays a couple of interesting trends in this temperature range that can be explained by several competing phenomena. Between 250 and 350 °C, the highest N₂ yield and NO_x conversion is achieved with a C₁:N of 6. The higher iBuOH doses at C₁:N of 9 and 12 actually decrease the NO_x conversion and N₂ yield. This optimum performance at a moderate reductant dose is likely due to SCR inhibition by the reductant species: at C₁:N greater than 6, the relatively high concentration of incoming reductant covers the catalyst surface and blocks active sites for NO SCR. Another interesting trend apparent in the N₂ yield plot is the dip in N₂ production observed at 325-350 °C at C₁:N ratios of 6 or greater. Comparing these results to the other N-species yield plots, it becomes apparent that this drop in N₂ yield coincides with an increase in NH₃ yield at the same temperatures. Further, the dip in N₂ yield is larger for the high reductant doses, which is consistent with the increasing NH₃ selectivity at higher C₁:N ratios. Over this moderate temperature range, higher iBuOH doses create a more reduced catalyst surface, which increases NH₃ selectivity at the expense of N₂ yield.

Above 350 °C, oxidation of reductant by O₂ to CO and CO₂ becomes prevalent, decreasing the coverage of reductant species on the catalyst surface. This shifts the selectivity of NO SCR back toward N₂, resulting in a drop off in NH₃ production and producing the second peak in N₂ yield for C₁:N ratios of 9 and 12 at 400°C. Meanwhile, the N₂ yield seen in the C₁:N = 6 curve decreases due to a lack of reductant at the higher temperatures. The diverse trends observed in this temperature range where SCR is most active point to the complexity of the reactions occurring during NO SCR by iBuOH over this catalyst.

Once the catalyst temperature reaches 450°C or above, NO₂ slip is once again observed for all C₁:N ratios, with higher yields observed as the ratio increases. Meanwhile, both N₂O and NH₃ yields are negligible in this temperature range regardless of the amount of iBuOH introduced to the catalyst. NO slip is significant even at high C₁:N ratios due to the lack of reductant availability, as most of the iBuOH is being oxidized directly to CO or CO₂ as shown in Figure 2.

The number of species observed during iBuOH-SCR illustrate that the chemistry occurring over the Ag/Al₂O₃ catalyst is both complex and different than typical HC-SCR without oxygenated reductants. The simultaneous presence of NO₂, N₂O, and NH₃ indicate that both oxidation and reduction are occurring over the catalyst under the same operating conditions. The formation of NH₃ is especially surprising due to the fact that reaction conditions are very lean with 10% O₂ in the simulated exhaust gas. The selectivity of the catalyst towards CO and NO₂ pose a potential emissions control challenge as both of these emissions are regulated and are being produced in concentrations high enough to cause concern. CO could be handled through a downstream oxidation catalyst, which would also help with reductant slip at lower temperatures and higher C₁:N ratios. The formation of N₂O is 35 ppm or less with an inlet concentration of 500 ppm NO, which is a level that may become significant under greenhouse gas emission regulations [31]. The NH₃ generated over the Ag/Al₂O₃ catalyst could be dealt with using an NH₃ slip catalyst such as those deployed in urea SCR systems, but the potential also exists for an

alternative solution. Fisher et al. and DiMaggio et al. have proposed the idea of a dual-SCR configuration, which utilizes an upstream Ag/Al₂O₃ catalyst and a downstream NH₃ SCR catalyst, such as a Cu-exchanged zeolite [3, 4]. At temperatures where peak NO_x conversion occurs over the Ag/Al₂O₃ catalyst, the NH₃ produced from NO_x reduction will be stored on the downstream NH₃ SCR catalyst. NO_x slipping through the Ag/Al₂O₃ catalyst when temperatures or reductant dosing are not ideal will then react with the NH₃ stored on the downstream NH₃ SCR catalyst, thus providing a two-stage solution to NO_x abatement during lean gasoline operation and expanding the potential window of operation and lowering the fuel penalty associated with the approach.

3.2 Comparison of iBuOH-SCR reactivity to EtOH-SCR

In order to provide a reliable basis for comparison, the EtOH-SCR data from previous work conducted with the same Ag/Al₂O₃ catalyst are included in Figure 4, which shows the NO_x reduction activity of EtOH for C₁:N ratios from 3 to 9 [9]. At temperatures below 275 °C, neither reductant is sufficiently active for SCR of NO to meet NO_x emissions standards, although iBuOH clearly outperforms EtOH at temperatures between 225-250 °C. Once the catalyst reaches 275 °C, both reductants approach peak SCR activity and convert 80% of incoming NO_x with sufficient reductant input. iBuOH is capable of reaching 90% NO_x conversion at 300°C, while the peak activity of EtOH begins 25 °C higher at 325 °C. Both reductants maintain this high level of SCR activity at evaluation temperatures up to 400 °C. Above this temperature, NO_x conversion falls to 30% or less at all three C₁:N ratios for iBuOH, while EtOH is still capable of reducing 80% of NO_x with C₁:N = 9 at 450°C before dropping to 30% at 500 °C. Interestingly, the uptick in conversion at 550°C for iBuOH-SCR is not observed for EtOH-SCR. This suggests that at 550°C the alkyl component of iBuOH is becoming active for SCR and leading to a small amount of NO_x reduction at elevated temperatures.

Although iBuOH has a wider temperature range for maximum NO_x conversion, it is important to note that the C₁:N ratios required to reach peak SCR activity over EtOH are lower. Optimal dosing would require C₁:N ratios of 6 and 9 to maintain >90% conversion between 300-400 °C for iBuOH, while EtOH can maintain this activity between 325-400 °C with C₁:N values of 3 and 4.5. This means that EtOH can provide excellent NO_x reduction performance with a smaller fuel penalty. For an inlet NO concentration of 500 ppm, the fuel penalty for EtOH is 4.5% lower for EtOH during peak NO_x conversion. While this 4.5% difference does not preclude the viability of iBuOH as a HC reductant in lieu of EtOH, it does represent a significant portion of the 10-20% fuel savings enabled by lean operation, and must be weighed against the aforementioned advantages of iBuOH as an alternative to EtOH.

The difference in NO_x conversion observed at identical C₁:N ratios for iBuOH and EtOH suggests that it could be the C-OH group in the alcohols which dictates SCR activity. With this in mind, the NO_x conversion of iBuOH and EtOH on the basis of C-OH:N ratio is plotted in Figure 5 for C-OH:N = 1.5 and 2.25. The reactivity of the two alcohol reductants is clearly much more similar when compared using C-OH:N ratio. The low temperature NO_x conversion of iBuOH is still superior, possibly due to the longer HC chain attached to the C-OH group in isobutanol being able to reduce the Ag into a more reactive state, but above 325 °C the two reductants show very comparable activity. Additionally, both reductants fall 25 °C short of reaching their full peak conversion window at C-OH:N = 1.5, but are capable of 90% conversion up to 400 °C when the C-OH:N ratio is increased to 2.25. Based on these trends, it seems likely that the C-OH group governs the SCR of NO when alcohols are used as the reductant.

EtOH conversion to CO and CO₂ during SCR over Ag/Al₂O₃ is shown in Figure 6. The reactivity of iBuOH initiates 50°C before EtOH. Both reductants reach 90% conversion at 400 °C and maintain this level of oxidation up to the maximum evaluation temperature of 550 °C. Low reactivity is an issue for both reductants at temperatures below 300 °C, and EtOH exhibits CO/CO₂ selectivity similar to that of iBuOH

[9]. Therefore, with regards to reductant slip and CO production, neither alcohol offers a significant advantage over the other.

With regards to nitrogen speciation during SCR of NO, both EtOH (not shown) and iBuOH exhibit similar trends overall, with some mild differences worth noting [9]. N₂O production with EtOH is nearly identical to that of iBuOH. The NH₃ generated when using EtOH is approximately 20% more than that observed with iBuOH, and requires lower C₁:N ratios to reach peak production. This means NH₃ slip is a larger issue with EtOH, but there is also greater potential for the implementation of the dual-SCR configuration discussed previously.

3.3 iBuOH/gasoline blends

3.3.1 iBuOH/gasoline blends: NO_x conversion

The NO_x conversion of both iBuOH/gasoline blends evaluated (iBu24 and iBu48) is shown in Figure 7 for C₁:N ratios of 6, 12, and 18, where C₁ refers to all carbon contained in the fuel blend, not just iBuOH. It must be noted that C₁:N ratios above 12 would correspond to untenable fuel penalties, and are only included in the evaluations to probe the limits of using iBuOH/gasoline blends as reductants for SCR of NO. The first blend evaluated was iBu24 (24% iBuOH/76% gasoline), which was chosen to represent the maximum expected blend limit for iBuOH in gasoline under current regulations for oxygenated components. Below 275 °C, iBu24 reduces less than 20% of the NO introduced to the catalyst, and C₁:N ratio has little impact on SCR activity. Between 300 and 400 °C, where pure iBuOH displays its peak NO_x reduction activity, some interesting trends occur as C₁:N ratio changes. At 300-325 °C, the NO_x conversion for C₁:N ratios of 6 and 12 is nearly identical, while C₁:N = 18 displays the worst SCR activity with 10-15% less NO_x reduction than the lower ratios. At 350 °C, the performance of C₁:N = 6 begins to decrease, and falls below C₁:N = 12 but is still above C₁:N = 18. Once the catalyst reaches 400 °C, NO_x conversion with C₁:N = 18 surpasses that of C₁:N = 6, but remains below that of C₁:N = 12. Throughout

this temperature range, where pure iBuOH reduced over 90% of incoming NO, NO_x conversion never reaches 60% with iBu24, even at the most active C₁:N ratio of 12. Above 450 °C, the SCR activity of the iBu24 blend surpasses that of pure iBuOH and improves with increasing C₁:N ratios, but this is due to the reactivity of gasoline species at higher evaluation temperatures through HC-SCR.

Due to the poor performance of iBu24, it is desirable to see if a higher blend level of iBuOH in gasoline could help improve NO_x conversion over Ag/Al₂O₃. The NO_x conversion curves in Figure 7 for iBu48 show many of the same general trends observed with iBu24, although overall performance is significantly improved at certain temperatures. Just as with iBu24, C₁:N ratio has minimal effect on NO_x reduction below 275 °C with iBu48, but conversion is approximately doubled in this range at the higher blend level. Between 300 and 400 °C the optimal performance is again obtained with C₁:N = 12, although with iBu48 the performance with C₁:N ratios of 6 and 9 remains nearly identical up to 350 °C. In the range of 300-350 °C increasing the C₁:N ratio to 18 severely inhibits SCR activity, with NO_x conversion limited to <50%. At 400 °C, the performance with C₁:N = 6 falls off, while the activity with C₁:N = 18 dramatically increases to match that of C₁:N = 12 with NO_x conversion approaching 85-90%. Trends above 450 °C match those observed during iBu24 evaluations, with stronger high temperature activity due to gasoline components and better activity with increased C₁:N ratios. However, even with iBu48 at double the anticipated blending limit, the catalyst never reaches the 90% NO_x conversion threshold with the iBuOH/gasoline blends evaluated in the current study. The poor performance of iBuOH/gasoline blends is unsurprising, as previous SCR performance evaluations by Pihl et al. found that using the gasoline in the current study as the only reductant over the Ag/Al₂O₃ catalyst results in low NO_x conversion across the evaluation temperature range, with a brief peak of 60% occurring at 500 °C [9].

3.3.2 iBuOH/gasoline blends: reductant conversion

In order to understand the impact of blending gasoline with iBuOH on the conversion of total reductant, Figure 8 contains CO, CO₂, and other organic species yields for iBuOH, iBu24, and iBu48 at a C₁:N ratio of 12. It should be noted that attempting to identify each individual organic species exiting the catalyst is challenging due to the complex nature of gasoline and the limited ability of an FTIR to quantify mixtures of organics, and therefore only CO and CO₂ yields are deemed to be accurately quantifiable. The predominant trend observed in Figure 8 is that the direct oxidation of reductant to CO and CO₂ is delayed until higher temperatures as gasoline blending level increases. This can be attributed to both the reduced SCR activity of the blends along with higher temperatures required to oxidize the less reactive HCs present in gasoline. Meanwhile, CO₂/CO selectivity remains essentially unchanged for iBuOH/gasoline blends versus pure iBuOH, and seems to be intrinsic to the Ag/Al₂O₃ catalyst.

3.3.3 iBuOH/gasoline blends: nitrogen speciation during SCR of NO

To further understand the impact of the iBuOH/gasoline blends on the NO SCR chemistry, the yields of the nitrogen-containing reactants/products when dosing reductants at a C₁:N = 12 are plotted in Figure 9. As with pure iBuOH, low temperature NO to NO₂ oxidation is observed with iBu24 and iBu48.

Decreasing iBuOH content in the blends has the effect of lowering peak NO₂ production and shifting this peak towards higher temperatures. N₂O yield has two distinct temperature windows for the blends. At temperatures up to 450 °C, the trends are nearly identical to that of pure iBuOH, although peak N₂O production decreases for lower iBuOH blend levels. From 500-550 °C, gasoline components become active for SCR and N₂O production actually increases for blends with higher gasoline content. Based on these results, it appears that N₂O production tracks NO_x conversion independent of which reductant is most active at a given temperature. NH₃ generation for both iBu24 and iBu48 is much lower than that of iBuOH, and the difference between the two blends is minimal across the evaluation temperature range.

3.3.4 iBuOH/gasoline blends: space velocity effects

While the NO SCR activity for the iBuOH/gasoline blends under the reaction conditions shown is well below that necessary to meet NO_x emission standards, the question remains as to whether the limitation on NO_x conversion is due to the chemistry of the reactions or if it is possible to improve the SCR activity by changing the conditions through the catalyst, such as by lowering GHSV. Thus, the SCR activity is measured at 10k, 17.5k and 35k h⁻¹ using iBu24 as the reductant at a C₁:N ratio of 12. As shown in Figure 10, decreasing the GHSV from 35k to 17.5k h⁻¹ leads to a significant SCR performance improvement of 10-30% in the temperature range from 275-450 °C, but conversion still reaches a maximum of only 85% at 450 °C. Further lowering the GHSV to 10k h⁻¹, it is possible to create a 100°C window between 350 and 450 °C where conversion is near or above 90%. This temperature window is shifted 50 °C higher than the peak performance observed when using pure iBuOH as the reductant. While this GHSV is much lower than is typically used in vehicle applications, it illustrates the potential for iBu24 as a HC reductant over Ag/Al₂O₃ if the catalyst monolith could be modified with higher washcoat loading or a larger size (i.e., higher cell density than the 62 cells/cm² being used).

3.4 Mechanistic aspects of iBuOH-SCR over Ag/Al₂O₃

While the current study is primarily focused on the performance and viability of iBuOH for use as a reductant for SCR of NO, it is reasonable to analyze the similarities observed between iBuOH SCR examined in the current investigation and EtOH SCR studied in previous research . During their research on EtOH-SCR over this Ag/Al₂O₃ catalyst, Pihl et al. observed the partial oxidation of EtOH to acetaldehyde coinciding with the oxidation of NO to NO₂ at temperatures preceding peak NO_x conversion by 50-75 °C [9]. It was proposed that these two species, or their adsorbed analogs, are key intermediates for EtOH-SCR. If SCR with iBuOH as the reductant follows an analogous mechanism, we would expect iso-butyraldehyde (CH₃CH₂CH₂CHO) (Figure 12) formation along with NO to NO₂ oxidation to precede NO_x reduction activity in the present research. However, a method for iso-butyraldehyde is

not included with the standard set of gas calibrations provided by the FTIR spectrometer manufacturer, so butyraldehyde measurements were used instead since the two have a similar IR spectrum. It should be noted that, due to the difficulty in measuring the wide range of hydrocarbon species produced during iBuOH-SCR, along with the lack of an actual iso-butyraldehyde method, the results presented for butyraldehyde measurements in this paper are meant to provide a qualitative understanding of what is occurring over the catalyst rather than strict quantitative results.

Measurements for the concentration of butyraldehyde and NO₂ during iBuOH-SCR evaluations using pure iBuOH are shown in Figure 11. Butyraldehyde formation begins at 150 °C and peaks between 200 and 250 °C, depending on C₁:N ratio. In this same temperature range we see NO₂ production, which reaches a maximum for all C₁:N ratios at 250 °C. This suggests that, when both iBuOH and NO are present, the partial oxidization of iBuOH to iso-butyraldehyde occurs simultaneous to the oxidation of NO to NO₂. As NO_x reduction activity begins in earnest at 275 °C, the concentrations of both butyraldehyde and NO₂ begin to rapidly decrease while NH₃ and N₂ begin to appear (Figure 3) during the peak SCR activity range for iBuOH between 300-400 °C. This process closely mirrors that seen by Pihl et al. with EtOH reductant over this same catalyst.

With these chemical transformations in mind, the following global reactions can be used to describe the observed products. At low temperatures (from 150-300 °C), partial oxidation of NO and iBuOH to NO₂ and iso-butyraldehyde occur according to reactions R10 and R11:

Between 300-500 °C the catalyst is active for the reduction of NO, and the intermediates formed in R1 and R2 further react to form N₂, NH₃, CO₂, and H₂O according to reactions R12-R14:

Above 500 °C SCR activity is diminished and the catalyst is dominated by the complete oxidation of iBuOH directly to CO₂ as shown in reaction R15:

Observing these products allows us to draw inferences regarding the possible surface chemistry occurring on the Ag/Al₂O₃ catalyst during iBuOH-SCR of NO, which likely mirrors the reaction mechanisms proposed for EtOH-SCR of NO. Johnson et al. investigated the EtOH-SCR mechanism by using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to examine the surface species appearing during SCR with EtOH on their own 2 wt% Ag/Al₂O₃ catalyst [18]. Nitrates were widely observed to cover the surface when feeding either NO₂ or NO+EtOH. Thus, under iBuOH-SCR conditions, where NO₂ formation is readily observed, it would follow that nitrates would be expected to cover the surface in this study as well. Johnson et al. also observed the formation of acetate on the surface

(CH_3COO^*) whenever ethanol was introduced in oxidizing environments. This acetate can readily desorb as acetaldehyde (CH_3CHO) through a surface reaction with adsorbed hydrogen [10, 32]. Although DRIFTS experiments were unable to be performed in this study, it is reasonable that iBuOH proceeds through a similar pathway, especially since butyraldehyde was observed in the effluent. In this case, iBuOH would readily form butyrate on the surface ($\text{CH}_3\text{CH}_2\text{CHCOO}^*$), which could react with a surface hydrogen (H^*) and desorb as iso-butyraldehyde ($\text{CH}_3\text{CH}_2\text{CHCHO}$).

These surface reactions agree with mechanisms proposed by other researchers, but what follows is still a matter of debate at this point [13, 16, 32-45]. These surface species provide a population of adsorbed NO_x species and reductants near the catalytic Ag sites, and also show a pathway to the formation of observed gas phase species, NO_2 and iso-butyraldehyde.

4. Conclusions

This study found that iBuOH can function as an effective reductant for NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$, with over 90% NO_x conversion observed at evaluation temperatures between 300 and 400 °C. Further, during peak SCR activity, the catalyst produces sufficient NH_3 to enable the possibility of using a dual SCR configuration with an NH_3SCR catalyst downstream of the $\text{Ag}/\text{Al}_2\text{O}_3$ HC-SCR catalyst. However, iBuOH/gasoline blends do not provide sufficient NO_x reduction activity unless the GHSV through the catalyst is significantly reduced, meaning higher loading, higher cell density, or a larger catalyst volume would be required for blends. When compared with EtOH as a reductant, iBuOH provides a broader temperature range for maximum NO_x conversion, but requires a higher fuel penalty to reach this peak activity. This difference in fuel penalty highlights the observation that the carbon and hydrogen molecules not in proximity to the -OH group do not participate in the SCR reactions directly and thus result in a higher concentration of spectator species that must be directly oxidized. On a volumetric basis, EtOH/gasoline blends outperform iBuOH/gasoline blends as reductants, but on an oxygen content basis both blends exhibit

similar SCR activity. Additionally, the formation of butyraldehyde and NO₂ at lower temperatures preceding NO_x reduction in the catalyst mirror the mechanism observed when using EtOH as a reductant, suggesting that the hydroxyl group in alcohols is the key component to NO SCR activity over Ag/Al₂O₃.

Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office. The authors gratefully acknowledge the support and guidance of program manager Kevin Stork at DOE.

Disclaimer

This manuscript has been authored by UT-Battelle, LLC, under Contract No. DEAC0500OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

References

- [1] S.C. Davis, S.W. Diegel, R.G. Boundy, Transportation Energy Data Book, 29th ed., 2010.
- [2] J.E. Parks, V. Prikhodko, W.P. Partridge, J.S. Choi, K. Norman, S. Huff, P. Chambon, SAE Int. J. Fuels Lubr. 3 (2) (2010) 956, also listed as SAE 2010-01-2267.
- [3] G.B. Fisher, C.L. DiMaggio, D. Trytko, K.M. Rahmoeller, M. Sellnau, SAE Int. J. Fuels Lubr. 2 (2010) 313, also listed as SAE 2009-01-2818.
- [4] C.L. DiMaggio, G.B. Fisher, K.M. Rahmoeller, M. Sellnau, SAE Int. J. Fuels Lubr. 2(2009) 66, also listed as SAE 2009-01-0277.
- [5] J. Breen, R. Burch, C. Hardacre, C. Hill, J. Phys. Chem. B 109 (2005) 4805.
- [6] R. Burch, J. Breen, C. Hill, B. Krutzsch, B. Konrad, E. Jobson, L. Cider, K. Eranen, F. Klingstedt, L. Lindfors, Top. Catal. 30 (1) (2004) 19.
- [7] R. Burch, Catal. Rev. Sci. Eng. 46 (2004) 271.
- [8] J.F. Thomas, S.A. Lewis, Sr., B.G. Bunting, J.M. Storey, R.L. Graves, P.W. Park, SAE Technical Paper Series 2005-01-1082 (2005).
- [9] J.A. Pihl, T.J. Toops, G.B. Fisher, B.H. West, Catal. Today 231 (2014) 46.
- [10] S.J. Schmieg, T.M. Sloane, R.J. Blint, SAE Technical Paper Series 2009-01-2819 (2009).
- [11] M.K. Kim, P.S. Kim, J.H. Baik, I.-S. Nam, B.K. Cho, S.H. Oh, Appl. Catal. B 105 (2011) 1.
- [12] P. Kyriienko, N. Popovych, S. Soloviev, S. Orlyk, S. Dzwigaj, Appl. Catal. B 140 (2013) 691.
- [13] Y. Yu, J. Zhao, Y. Yan, X. Han, H. He, Appl. Catal. B 136 (2013) 103.

- [14] A. Flura, X. Courtois, F. Can, S. Royer, D. Duprez, *Top. Catal.* 56 (1–8) (2013) 94.
- [15] N. Popovych, P. Kirienko, S. Soloviev, S. Orlyk, *Catal. Today* 191 (1) (2012) 38.
- [16] Y. Yan, Y. Yu, H. He, Z. Hong, *J. Catal.* 293 (2012) 13.
- [17] E. Sayah, C. La Fontaine, V. Briois, D. Brouri, P. Massiani, *Catal. Today* 189 (1)(2012) 55.
- [18] W.L. Johnson II, G.B. Fisher, T.J. Toops, *Catal. Today* 184 (1) (2012) 166.
- [19] M. Boutros, J.M. Trichard, P. Da Costa, *Catal. Today* 52 (13–20) (2009) 1781.
- [20] R. da Silva, R. Cataluna, A. Martinez-Arias, *Catal. Today* 143 (3–4) (2009) 242.
- [21] Q. Wu, H. He, Y.B. Yu, *Appl. Catal. B* 61 (1–2) (2005) 107.
- [22] M.D. Kass, J.F. Thomas, S.A. Lewis Sr., J.M. Storey, N. Domingo, R.L. Graves, *SAE Technical Paper Series* 2003-01-3244 (2003).
- [23] J. Baustian, L. Wolf, *SAE International* 2012-01-1741, 2012.
- [24] <http://www3.epa.gov/otaq/fuels/renewablefuels/> (December 17, 2015).
- [25] Code of Federal Regulations: Protection of the Environment, Title 40 CFR Part 80, U.S. Environmental Protection Agency (2015).
- [26] G. Karavalakis, D. Short, D. Vu, R.L. Russell, A. Asa-Awuku, H. Jung, K.C. Johnson, T.D. Durbin, *Energy* 82 (2015) 168.
- [27] C. Sayin, M.K. Balki, *Energy* 82 (2015) 550.
- [28] A. Elfasakhany, *Energy Convers. Manage.* 95 (2015) 398.
- [29] A. Irimescu, *Energy* 36 (2011) 3030.

- [30] J.M. Herreros, P. Geroge, M. Umar, A. Tsolakis, Chem. Eng. J. 252 (2014) 47.
- [31] Rules and Regulations, 79 Federal Register 81 (April 28, 2014).
- [32] Y. Yeom, M. Li, W. Sachtler, E. Weitz, J. Catal 238 (2006) 100.
- [33] T. Chafik, S. Kameoka, Y. Ukisu, T. Miyadera, J. Mol. Catal. A: Chem. 136 (1998) 203.
- [34] Y. Yeom, M. Li, W. Sachtler, E. Weitz, J. Catal. 246 (2007) 413.
- [35] Y. Yu, X. Song, H. He, J. Catal 271 (2010) 343.
- [36] H. He, X. Zhang, Q. Wu, C. Zhang, Y. Yu, Catal. Surv. Asia 12 (2008) 38.
- [37] H. He, Y. Yu, Catal. Today 100 (2005) 37.
- [38] K. Arve, E. Popov, F. Klingstedt, K. Eranen, L. Lindors, J. Eloranta, D. Murzin, Catal. Today 100 (2005) 229.
- [39] N. Bion, J. Saussey, M. Haneda, M. Daturi, J. Catal 217 (2003) 47.
- [40] Y. Yu, H. He, Q. Feng, H. Gao, X. Yang, Appl. Catal. B 49 (2004) 159.
- [41] S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, J. Catal 276 (2010) 49.
- [42] S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, J. Catal 281 (2011) 98.
- [43] A. Mhadeshwar, B. Winkler, B. Eiteneer, D. Hancu, Appl. Catal. B 89 (2009) 229.
- [44] W. Qiang, Y. Yunbo, H. Hong, Chin. J. Catal. 27 (2006) 993.
- [45] S. Tamm, H. Ingelsten, A. Palmqvist, J. Catal. 255 (2008) 304.

Table 1. Gas composition during C₁:N sweep with iBuOH.

C ₁ :N	iBuOH (ppm)	NO (ppm)	O ₂ (%)	H ₂ O (%)
3	375	500	10	5
4.5	562.5	500	10	5
6	750	500	10	5
9	1125	500	10	5
12	1500	500	10	5

Table 2. Properties of gasoline used in current study based upon certificate of analysis provided by Haltermann Solutions Inc.

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

Figure 1. NO_x conversion over Ag/Al₂O₃ with pure iBuOH as the reductant at C₁:N ratios between 3 and 12 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹.

Figure 2. Steady state carbon yields for a) CO, b) CO₂, c) C₃H₇CHO, and other HCs over Ag/Al₂O₃ with pure iBuOH as the reductant at $C_1:N$ ratios between 3 and 12 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹.

Figure 3. Steady state nitrogen yields for a) NO, b) NO₂, c) N₂O, d) NH₃, and e) N₂ over Ag/Al₂O₃ with pure iBuOH as the reductant at $C_1:N$ ratios between 3 and 12 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹.

Figure 4. NO_x conversion over Ag/Al₂O₃ with pure EtOH as the reductant at C₁:N ratios between 3 and 9 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹ [9].

Figure 5. NO_x conversion over Ag/Al₂O₃ with iBuOH and EtOH at a) C-OH:N = 1.5 and b) C-OH:N = 2.25 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹ [9].

Figure 6. Ethanol conversion to CO and CO₂ over Ag/Al₂O₃ with pure EtOH as the reductant at C₁:N ratios between 3 and 9 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹ [9].

Figure 7. NO_x conversion over $\text{Ag}/\text{Al}_2\text{O}_3$ with a) iBu24 and b) iBu48 as the reductant at $C_1:N$ ratios between 6 and 18 in an exhaust flow with 500 ppm NO , 10% O_2 , 5% H_2O and N_2 balance between 150-550°C at $\text{GHSV} = 35,000 \text{ h}^{-1}$.

Figure 8. Steady state carbon yields for a) CO, b) CO₂, and c) other HCs over Ag/Al₂O₃ with iBuOH, iBu48, and iBu24 reductants at C₁:N = 12 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹.

Figure 9. Steady state nitrogen yields for a) NO, b) NO₂, c) N₂O, d) NH₃, and e) N₂ over Ag/Al₂O₃ while feeding iBuOH, iBu48, or iBu24 as the reductant at C₁:N = 12 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C at GHSV = 35,000 h⁻¹.

Figure 10. Impact of varying GHSV on NO_x conversion over Ag/Al₂O₃ with iBu24 as the reductant at C₁:N = 12 in an exhaust flow with 500 ppm NO, 10% O₂, 5% H₂O and N₂ balance between 150-550°C.

Figure 11. Concentration of a) butyraldehyde and b) NO_2 during SCR over Ag/Al_2O_3 with pure iBuOH as the reductant at $C_1:N$ ratios between 3 and 12 in an exhaust flow with 500 ppm NO, 10% O_2 , 5% H_2O and N_2 balance between 150-550°C at GHSV = 35,000 h^{-1} .

iBuOH

Iso-butyraldehyde

Figure 12. Diagram of isobutanol and iso-butyraldehyde molecules.