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Improved NOx reduction over the staged Ag/Al_2O_3 catalyst system

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ABSTRACT

The reaction mechanism of reducing NOx with hydrocarbons over Ag/Al_2O_3 has been examined to improve its NOx reduction performance at lower temperatures, using ethanol and *n*-octane as representative hydrocarbon reductants. Based on the results obtained at the early stages of the hydrocarbon oxidation and NO reduction, it is proposed that the partial oxidation of hydrocarbons and the oxidation of NO are the first reaction steps over Ag/Al_2O_3. *n*-Octane is broken up into smaller hydrocarbon molecules, which are then subsequently oxidized to form various aldehydes, while ethanol is also rapidly converted to acetaldehyde. At the same time, NO is oxidized effectively to NO_2 in the presence of reductants.

These observations and additional experiments with variable amounts of Al_2O_3 placed downstream of the Ag/Al_2O_3 catalyst suggest that the NO reduction by hydrocarbons over Ag/Al_2O_3 may occur via a bifunctional reaction mechanism; NO and hydrocarbons are converted into NO_2 and more reactive hydrocarbon species (i.e., smaller alkenes, oxygenated hydrocarbons), respectively, over the Ag sites, while N_2 is produced from the subsequent reactions between these intermediate species over different sites including Al_2O_3.

The proposed bifunctional reaction mechanism offers an opportunity to improve the overall NOx reduction performance of Ag/Al_2O_3 by optimizing individual reaction steps separately. Thus, the concept of a staged catalyst system has been examined using Ag/Al_2O_3 for the formation of reaction intermediates, and a secondary catalyst (e.g., Al_2O_3 or BaY) for the subsequent N_2 production reaction. Significant improvement in NOx reduction to N_2 was obtained at lower temperatures, when BaY was used as the second catalyst and ethanol was used as reductant.

1. Introduction

1.1. Selective catalytic reduction of NOx by hydrocarbon

Diesel engines can offer substantially higher fuel efficiency, good driving performance, and reduced carbon dioxide emission compared to stoichiometric gasoline engines. For these reasons along with favorable taxation policies, diesel-powered passenger vehicles have been gaining popularity in Europe in recent years. Despite the increasing public demand for higher fuel economy and reduced dependency on imported oil, however, the lack of effective and affordable methods for meeting the future emission standards has delayed the introduction of these fuel-efficient engines to the US market.

Since diesel engines operate with excess oxygen, it is difficult to reduce nitrogen oxides ($NOx = NO + NO_2$) in the exhaust with the traditional three-way catalyst (TWC), which has been used successfully for stoichiometric gasoline engines. One of the technologies considered to-date is the use of catalysts that can selectively reduce NOx using engine-out hydrocarbons (HC-SCR). But, despite the intensive search for a new class of materials that promote the reaction between the engine-out hydrocarbons and NOx over the competing combustion reaction, the commercial application of this technology has not been successful because of poor activity, narrow operating temperature window, and insufficient durability [1].

An alternative to the use of engine-out hydrocarbons as the only source of reductant is to inject an appropriate reducing agent into the exhaust, which can reduce NOx more efficiently. In fact, the SCR of NOx using ammonia as the reductant (NH_3–SCR) has been used commercially for stationary applications since the 1970s. Because of the challenges associated with storage, handling and transportation of NH_3, the use of aqueous urea solution has been explored as a storage compound of NH_3 for mobile applications. For example, the SCR of NOx using urea (urea-SCR) is currently being considered as the primary NOx control technology for meeting the future emission standards (e.g., Tier 2 Bin 5, Euro 6) by many automakers in Europe and North America.

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Although typical hydrocarbons present in engine exhaust are generally less active and selective than ammonia, the NOx reduction efficiency of HC-SCR catalysts can be greatly improved if appropriate hydrocarbon species are used as reductant. For example, partially oxidized hydrocarbon species, such as acetaldehyde (CH_3CHO) and ethanol (C_2H_5OH), have been found to be very effective for reducing NOx over γ-alumina [2], NaY, BaY [3], and Ag/Al_2O_3 [4–7]. In particular, Ag/Al_2O_3 has received considerable attention over the past several years for its excellent NOx reduction activity with various hydrocarbon reductant species including alcohols and heavy fuel-component hydrocarbons [8,9]. However, the light-off temperature of Ag/Al_2O_3 for NO reduction is still too high to be used for light-duty diesel applications, although it has been reported that low-temperature activity can be promoted with the addition of H_2 [10]. It also produces unwanted harmful byproducts (e.g., NH_3, HCN, CH_3CHO) under certain reaction conditions [11].

This study is aimed at improving the NOx reduction performance of Ag/Al_2O_3 catalyst by elucidating the reaction mechanism. The catalyst behavior at the early stages of the hydrocarbon oxidation and NO reduction was probed using two representative hydrocarbon species as reductant: ethanol (i.e., oxygenated HC) and *n*-octane (i.e., fuel-component HC). The mechanistic understanding led to the concept of using a staged Ag catalyst system to improve NOx conversion to N_2.

1.2. NOx reduction mechanism over Ag/Al_2O_3

1.2.1. NOx reduction by ethanol

There have been a few previous studies devoted to the reaction mechanism of NOx reduction by ethanol [7,12–14]. It has been suggested that NO and C_2H_5OH are initially converted to surface NOx species (NOy) and CxHyOz (e.g., acetate), respectively. These oxidized species subsequently react to form various organic nitro species (e.g., R–NO_2, R–ONO), which decompose to isocyanate (–NCO) and/or cyanide (–CN) species on the catalyst surface before producing N_2 [7].

Alternatively, the partial oxidation of ethanol to acetaldehyde has been proposed as an important initial step during the NO reduction by ethanol [12]. Ethanol was converted to acetaldehyde and CO_2 in the presence of 10% O_2, or C_2H_4 in the absence of O_2. When the NO reduction activity was compared using different alcohols as reductant (e.g., ethanol, 1-propanol, 2-propanol, and methanol), 1-propanol (straight-chain alcohol) was found to be as effective as ethanol for reducing NO. Interestingly, significant amounts of NO could be reduced by ethanol or acetaldehyde only in the presence of 10% O_2. So it was suggested that NOx is reduced by oxidation products of acetaldehyde.

In a recent *in situ* diffuse reflectance FT-IR spectroscopy (DRIFT) study of NO reduction by ethanol, the formation of a ring structure enolic species ($CH_2CHCHCHO^-$) was observed on Ag/Al_2O_3, which was supported by density functional theory (DFT) calculations [13,14]. The adsorbed enolic species was also found to be more prone to react with NO + O_2 compared to acetate. Based on the results of temperature-programmed desorption (TPD) experiments, it was suggested that enolic species is formed from the aldol condensation reaction of a partial oxidation product of ethanol (i.e., acetaldehyde) on the catalyst surface. However, considering the reverse aldol condensation reaction occurring in the presence of water, it is unlikely that acetaldehyde will form enolic species under realistic exhaust conditions, which contain a large concentration of water vapor. Instead, acetaldehyde is more likely to be oxidized to surface acetate by NOy species, and then further to –NCO and/or –CN species over Al_2O_3. The formation of N-containing organic species like nitromethane (CH_3NO_2) and nitrosomethane (CH_3NO), and the formation of N_2 from these N-containing species have been reported over Cu-ZSM-5 [15] and Co-ZSM-5 [16,17].

1.2.2. NOx reduction by n-octane

Among the few published reports on the reaction mechanism of NOx reduction by heavy hydrocarbons over Ag/Al_2O_3, acetate (CH_3COO^-) and nitrates ($NO_3{}^-$) species were observed during the in situ FT-IR experiments of NO reduction by *n*-hexane, and nitrates were found to be reactive toward *n*-hexane only in the presence of O_2 [18]. This led to the mechanistic hypothesis that partially oxidized hydrocarbon species like acetate are produced from *n*-hexane, which subsequently react with nitrates to form organic nitro compounds, which then decompose to –NCO and –CN before producing N_2. In addition, a structure–activity relationship was clarified during the NOx reduction by *n*-octane. UV–vis and Ag K-edge XAFS results indicated that highly dispersed Ag^+ ions are predominant Ag species below 2 wt.% Ag loading, while Ag_n clusters are primarily formed at higher Ag loadings. It was suggested that highly dispersed Ag^+ ions are the active sites for the reduction of NO to N_2, while the Ag_n clusters are responsible for the hydrocarbon combustion as well as N_2O formation via NO decomposition reaction [18].

In addition to the reaction occurring on the catalyst surface, a gas-phase reaction between the species created over the Ag/Al_2O_3 surface was suggested to be important during the NO reduction by *n*-octane [19]. When a commercial Pt-based oxidation catalyst was placed immediately behind Ag/Al_2O_3 as a clean-up catalyst to remove CO and unburned hydrocarbons, NOx conversion to N_2 was decreased dramatically. As the distance between the two catalysts was increased, the conversion was gradually recovered, which suggested that the gas residence time behind the Ag catalyst (which determines the extent of the gas-phase reaction) might be an important design parameter for Ag/Al_2O_3-based lean NOx control systems.

2. Experimental

2.1. Catalyst preparation and characterization

Ag/Al_2O_3 containing 1.0 and 2.0 wt.% Ag were prepared on a commercial γ-Al_2O_3 powder (Sasol, Catalox SBa-200, BET surface area = 197 m^2/g) by the incipient wetness method using $AgNO_3$ (JT Baker) as a precursor. The catalyst samples were dried at 110 °C overnight and calcined at 500 °C for 4 h. The Sasol's γ-Al_2O_3 powder contained low levels of impurities (e.g., Na_2O, TiO_2, and SiO_2), and was calcined at 550 °C for 4 h prior to the use. Both XRD and X-ray photoelectron spectroscopy (XPS) analyses indicated that highly dispersed Ag^+ ions were predominant Ag species below 2 wt.% Ag loading in agreement with the literature [18].

BaY containing 17.0 wt.% Ba was prepared from the NaY powder (Zeolyst, CBV-100, 10 wt.% Na, Si/Al = 5.1) by the ion exchange method using $Ba(NO_3)_2$ (JT Baker) as a precursor at room temperature for 24 h. The sample was then dried at 120 °C for 4 h, and calcined at 550 °C for 4 h. This ion exchange and calcination steps were repeated four times. The concentrations of Ag and Ba reported here were determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES).

2.2. Catalyst performance evaluation

All the experiments were conducted in a vertical micro reactor system with the feed gas flowing downward. Catalyst samples of 60–80-mesh size were loaded in a 3/8 in. OD quartz tube, which