Bi-functional Hydrocarbon SCR Catalyst

Dan Hancu,*,[1] Donald Whisenhunt,[1] Ben Winkler,[1] Oltea Siclovan,[1] Larry Lewis,[1]
Ashish Mhadeshwar, [1] Andrew Gordon,[2] Burapat Inceesungvorn,[2] Vladimir
Demidyuk,[2] Christopher Hardacre,[2] Robbie Burch,[2]

(1) GE Global Research, 1 Research Circle, Niskayuna, NY 12301
(2) CenTACAT, Queen's University of Belfast, Belfast, BT9 5AG, U.K.
*hancuda@crd.ge.com

Introduction

NO selective catalytic reduction (SCR) with diesel derived reductants over Ag/Al_2O_3 catalysts has received much attention, as it provides the opportunity to remove nitrogen oxides from Diesel exhaust without an urea infrastructure.[1] The technology explored here involves on-board conversion of a slip-stream of fuel into smaller hydrocarbons (C_2-C_8), followed by the SCR reaction of the resulting hydrocarbon mixture with NOx over a Ag-based catalyst. The reaction stream resulted from converting fuel is a complex mixture of saturated, and unsaturated hydrocarbons. Ag/Al_2O_3 catalysts are very sensitive to the nature of the hydrocarbon reductant with the following ascending order in activity: C_1 << C_2-C_4 alkenes < C_6-C_8 aliphatics (T = 275 – 425 ^oC). Therefore, it is desired to improve Ag/Al_2O_3 activity with small alkenes while maintaining the reactivity for higher aliphatics in order to increase its overall catalytic efficiency with converted diesel fuel. In the current study, we describe the development of a bi-functional hydrocarbon SCR catalyst with improved performance using simulated converted diesel fuel as a NOx reductant. The approach involved the following sequential steps: (a) catalyst discovery by parallel testing of libraries Ag/Al_2O_3 - zeolites in single and dual bed configuration, (b) parametric studies in the bench scale reactor, and (c) mechanistic studies using diffuse reflectance infra-red Fourier Transform spectroscopy (DRIFTS).

Materials and Methods

Commercially available zeolite materials with different cage size structure (Mordenite, Beta, ZSM-5, Ferrierite) were tested together with the 2% Ag /Al_2O_3 catalyst in single, dual bed, and mixed configuration, where the total weight of material was held constant. Two methods were used to deposit the metals onto the supports. First, chemical ion exchange was used with zeolite materials (Cu, Fe, Pd, Pt), while Ag (2 % mol.) was deposited on the alumina support (Norton) by incipient wetness technique. Catalyst discovery was performed in a 32-tube parallel testing reactor. Catalysts were sulfur pretreated with 7% H_2O, 12 % O_2, and 50 ppm SO_2 for 7 h at 450 ^oC. The reductants used were mixtures of C_2-C_8 hydrocarbons: **C_2-C_3 fraction** (ethylene (50%), propylene (50%)), and **C_8 fraction** (2,2,4-trimethylpentane (60%), octane (10%), toluene (30%)). The adsorbed species on the catalysts were analyzed under the same reaction conditions in a DRIFTS setup which consisted of an in-situ high temperature diffuse reflectance IR cell (Spectra-Tech) fitted with ZnSe windows; the cell has been modified in house to behave as a plug flow reactor [2] and holds 50±5mg of catalyst. All spectra have been referenced to the fresh catalyst under Ar.
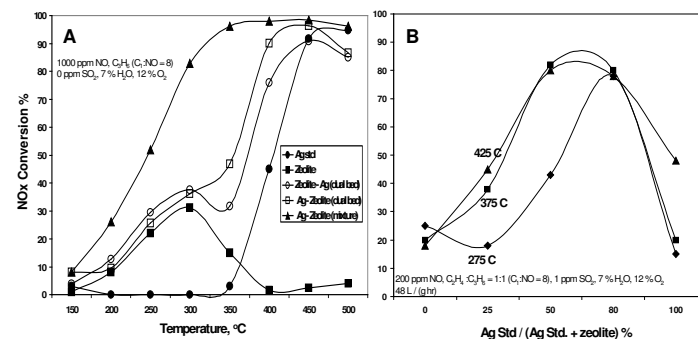
Figure 1 SCR performance of 2 % Ag/Al_2O_3 – Ferrierite bi-functional catalyst with C_2-C_3 fraction: (**A**) Single, and dual beds comparison. (**B**) Effect of zeolite content on the SCR performance in the 2 % Ag/Al_2O_3 – Ferrierite mixture

Results and Discussion

A 12-member library of Ag/Al_2O_3–zeolite system was tested in the presence of two hydrocarbon mixtures (**C_2-C_3 fraction** and **C_8 fraction**) to simulate the reaction mixture produced from a diesel conversion process. Low T performance with **C_2-C_3 fraction** was improved when Ag/Al_2O_3 was physically mixed with Ferrierite. As shown in Figure 1 (**A**), the following ascending NOx reduction efficiency was determined at T = 300 ^oC: Ag Std (5 %) << Ferrierite (30 %) < Dual bed [Ag/Al_2O_3–Ferrierite] ~ Dual bed [Ferrierite–Ag/Al_2O_3] (35 %) << Mixture [Ag/Al_2O_3 – Ferrierite] (80 %). When zeolite content was varied in the Ag-zeolite solid mixture, the NO_x removal efficiency reached a maximum (80%) for Ag/Al_2O_3 : H-Ferrierite = 4:1 (wt.), at T = 275 – 425 ^oC. The synergetic effect is not observed for propane, or the **C_8 fraction** at any zeolite-Ag/Al_2O_3 composition. The DRIFTS spectra for the **C_2-C_3 fraction** found in the case of the 2% Ag /Al_2O_3 catalyst shows strong features between 1200-1600 cm^{-1} associated with nitrates, carbonates and carboxylates. In the mixed bed of the zeolite and silver catalyst, an additional very strong feature is observed at ~1700 cm^{-1} which is also observed when the zeolite is studied in the absence of the silver catalyst. This feature is also observed in the absence of NO and may be associated with the selective oxidation of the olefin to form, e.g., a carbonyl molecule. A possible mechanism for the enhanced activity in the mixed bed system is that the intimate contact of the zeolite and silver catalyst allows trapping and reaction of the oxygenated molecule by the silver catalyst. Oxygenates [3] are more active for the SCR reaction compared with the alkene hence the low temperature SCR activity.

Significance

Bi-functional Ag/Al_2O_3-Ferrierite catalyst mixture has improved performance with small unsaturated hydrocarbons (C_2-C_3), increasing the overall NO_x removal efficiency with converted Diesel fuel at low exhaust temperatures (< 400 ^oC).

References
[1] Burch, R.; Breen, J.P.; Meunier, F.C. Appl. Catal. B, 2002, 39, 283 and references therein.
[2] Meunier, F. C.; Goguet, A.; Shekhtman, S.; Rooney, D.; Daly, H., Appl. Catal. A, 2008, 340, 196.
[3] Yu, Y.B.; He, H.; Feng, Q.C.; Gao, H.W.; Yang, X., Appl. Catal. B 2008, 49 159.