Studies of the mechanisms for NOx reduction with oxygenate additives.

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Introduction
The reduction of NOx in diesel exhaust is an important chemical problem that is directly relevant to current societal environmental concerns. Though it is well known that additives such as ammonia, and more recently acetaldehyde (AA) [1], can reduce NOx under conditions that correspond to those found in diesel exhaust, the operative chemistry in such systems can be quite complex. As such, delineating a detailed microscopic mechanism for these NOx reduction processes is challenging, but significant progress is being made in this area.

We have been investigating the mechanism for NOx reduction involving AA, ammonia, and more recently ethanol, as additives under conditions that are relevant to diesel exhaust.[2-4] Though AA is an effective reductant for NOx [1,2], ethanol is a desirable additive in that it is inexpensive and relatively benign when compared to some other proposed additives. Our work on ethanol has focused on delineating the mechanism for NOx reduction with this reductant, and on understanding the effect of different catalysts on the kinetics and mechanism for NOx reduction with ethanol.

This presentation will focus on our mechanistic studies of NOx reduction with these additives. The emphasis will be on similarities and differences in the mechanism for NOx reduction with acetaldehyde and ethanol (EtOH) over different catalysts: specifically, BaNa/Y (AA), Ag/Y (EtOH) and Ag/γ-Al2O3 (EtOH).

Materials and Methods
Our mechanistic studies have employed FTIR, and in some cases rapid scan FTIR, to study reaction intermediates and reactions taking place on zeolite and γ-alumina catalysts. FTIR studies of these catalyst samples have been performed in a transmission mode using a temperature controlled "wire grid" reactor [2,5]. We have also employed flow reactor studies, where the products of reaction can be monitored with a GC or mass spectrometer. Identification of intermediates has been aided by the use of isotopically labeled reagents.

Results and Discussion
We have elucidated the multi-step mechanism for the reduction of NOx in the presence of ethanol over silver exchanged zeolite Y (Ag/Y). Ethanol reacts with O2 and/or NO2 to form AA at temperatures as low as 200 °C. Surface acetate ions, formed from the oxidation of AA, react with NO2 to yield nitromethane; a critical intermediate in subsequent deNOx chemistry. Nitromethane, which is likely in equilibrium with its aci-anion, reacts with NO2. Our data for the systems studied suggest that this reaction leads to a dinitromethane intermediate, which then dissociates to form HNCO. HNCO is hydrolyzed to form ammonia, which reacts with nitrous acid to form ammonium nitrite; a compound that is known to readily decomposes at typical NOx reduction temperatures to yield N2. For ethanol over Ag/Y, CN-, NC- and NCO- are intermediates which are likely bound to silver ions. These data from this study and prior studies [2,4] of deNOx reactions allow us to compare the kinetics and mechanism for deNOx reactions taking place on Ag/Y and Ag/γ-Al2O3. We find that the major qualitative difference in these systems is the temperature dependence of the reaction of acetate with NO2. Accordingly, the N2 yield at 200 °C is much higher over Ag/Y than over Ag/γ-Al2O3. Since the deNOx mechanism with ethanol as a reductant proceeds through an AA intermediate these data can also be compared to data for NOx reduction with AA over BaNa/Y. The temperature dependence of the reaction of surface bound acetate with NO2 is again a factor in the yield for NOx reduction.

Pretreatment of Ag/Y, with O2 or H2 does not affect the yield of N2. The yield of N2 for deNOx reactions with ethanol as an added reductant approaches 60%, and remains constant for at least five hours on stream, making this catalyst promising for NOx reduction.

Significance
NOx reduction in diesel exhaust is an interesting, complex and important chemical problem that has a direct impact on environmental problems in the world today. Studies in our group have yielded detailed mechanistic information on the pathways for NOx reduction using added reductants. This report will discuss similarities and differences in the mechanisms for NOx reduction over different catalysts with two oxygenate additives (AA and EtOH). These results provide detailed information on the reaction mechanism(s) that are necessary for efficient NOx reduction as well as identifying the rate limiting step(s) in these mechanisms.

References