

Studies of the mechanisms for NO_x reduction with oxygenate additives.

Younghoon Yeom, Meijun Li, Wolfgang Sachtler and Eric Weitz*
Institute for Catalysis and Energy Processes and Department of Chemistry, Northwestern
University, Evanston, IL, USA, 60208

* weitz@northwestern.edu

Introduction

The reduction of NO_x 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 NO_x 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 NO_x reduction processes is challenging, but significant progress is being made in this area.

We have been investigating the mechanism for NO_x 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 NO_x [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 NO_x reduction with this reductant, and on understanding the effect of different catalysts on the kinetics and mechanism for NO_x reduction with ethanol.

This presentation will focus on our mechanistic studies of NO_x reduction with these additives. The emphasis will be on similarities and differences in the mechanism for NO_x 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 NO_x 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 deNO_x 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 NO_x 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 deNO_x reactions allow us to compare the kinetics and mechanism for deNO_x 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 deNO_x mechanism with ethanol as a reductant proceeds through an AA intermediate these data can also be compared to data for NO_x 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 NO_x reduction.

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

Significance

NO_x 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 NO_x reduction using added reductants. This report will discuss similarities and differences in the mechanisms for NO_x 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 NO_x reduction as well as identifying the rate limiting step(s) in these mechanisms.

References

1. Panov G., Tonkyn R.G., Balmer M.L., Peden C.H.F., Malkin A. and Hoard J.W., *Soc. Automot. Eng.* **2001**-01-3513
2. Yeom Y., Wen B., Sachtler W.M.H. and Weitz E. *J. Phys. Chem., B*, **108** 5386 (2004)
3. Yeom Y., Henao J., Li M., Sachtler W.M.H., and Weitz E., *J. Catal.* **231**, 181. (2005)
4. Yeom Y., Li M., Sachtler W. M.H., and Weitz E., *J. Catal.* **238** 110. (2006)
5. Basu P., Ballinger T.H., and Yates J.T., *Rev. Sci. Instrum.* **59**, 1321 (1988)