

The Co-adsorption of NO and C₂H₄ on Rh-loaded CeO_x(111)

D.R. Mullins and K. Zhang (Oak Ridge National Laboratory)

Abstract No. Mull2018

Beamline(s): U12A

Introduction: Several studies have demonstrated that Rh supported on reduced CeO_x thin films has a much higher activity for promoting the decomposition of NO compared to the reaction of NO on bulk Rh. This activity has the potential for enhancing the catalytic reduction of NO in automotive exhaust catalysts. As NO decomposes, the CeO_x becomes more oxidized and ultimately the enhanced Rh activity disappears. In order to maintain the enhanced activity, a reductant must also be present in order to reduce the CeO_x. We have studied NO and C₂H₄ and have determined how these co-adsorbates interact with each other and with the ceria substrate.

Methods and Materials: Highly ordered CeO_x(111) films were prepared by evaporating Ce onto Ru(0001) in an oxygen ambient of ca. 10⁻⁸ torr. The oxidation state of the ceria was controlled by adjusting the O₂ pressure and determined from the Ce 4d core-level spectra. Sub-monolayer amounts of Rh were evaporated onto the ceria surface. The sample was then exposed to C₂H₄ at 150 K followed by NO at 200 K. Surface intermediates were determined from C 1s and N 1s core-level spectra after heating to different temperatures.

Results: When NO and C₂H₄ are co-adsorbed on Rh / CeO₂ there are no surface intermediates formed that indicate a direct interaction between the NO and the C₂H₄. The C 1s spectra (left) indicate that C₂H₄ progressively dehydrogenates at higher temperatures. The N 1s spectra (not shown) indicate NO decomposition as the temperature is raised. N₂, NO, CO and H₂O along with a small amount of CO₂ are produced, however, during thermal desorption. Most of the CO results from the reaction of the C from C₂H₄ with the O from the CeO₂ and is the first reaction we have studied in UHV that is capable of substantially reducing the ceria.

When NO and C₂H₄ are co-adsorbed on Rh / CeO_x, different types of C-N fragments are formed on the surface as indicated by the C 1s spectra (right). Initially, CN species are formed between 400 K and 500 K. At higher temperatures these fragments combine to form more complex C_xN_y structures. These structures produce two different peaks in the C 1s spectra, which are labeled C_xN_y(I) and C_xN_y(II). The difference in the binding energy between these two peaks is related to the number of N atoms bound to the C and / or to the hybridization between the C and the N.

Acknowledgments: Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

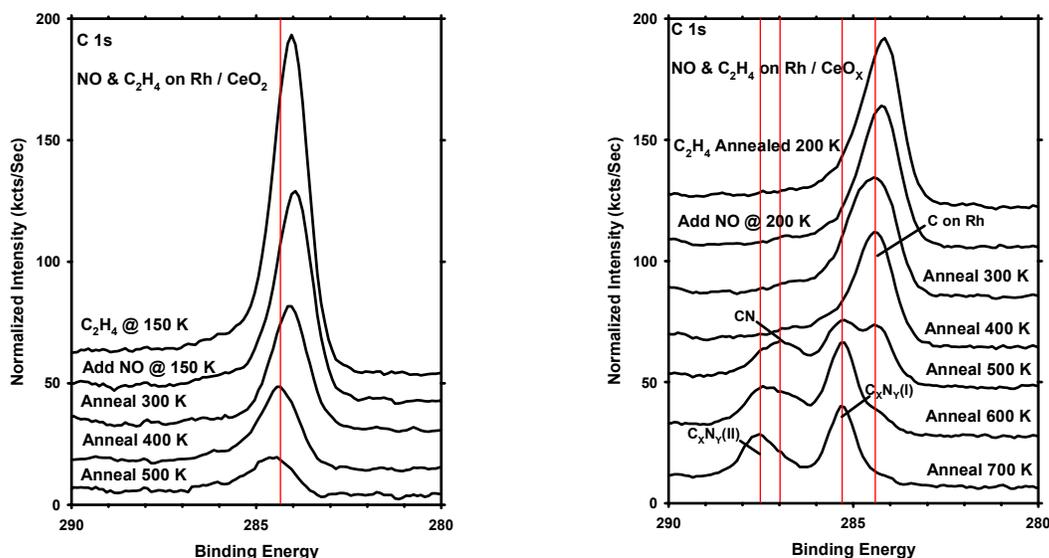


Figure 1. C 1s spectra from NO and C₂H₄ co-adsorbed on Rh / CeO₂ (left) and Rh / CeO_x (right) and annealed as indicated.