

Mid- and Far-Infrared Reflection/Absorption Spectroscopy (IRAS) Studies of NO on Rh Single Crystal Surfaces

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Introduction: The NO/CO reaction over Rh metal in automobile catalytic converters is critical to the control of emissions of these pollutant molecules. As part of a program to determine the elementary mechanism(s) of this reaction, we have been performing mid- and far-infrared reflection/absorption spectroscopic (IRAS) measurements of the adsorption and co-adsorption of NO and CO on Rh single crystal surfaces. Of particular interest is the low-frequency range of the IRAS spectra where we hoped to observe features due to metal-N stretching and/or bending vibrational motions. In particular, we hoped to obtain information regarding the site-requirements for the dissociation of the NO molecule on various Rh single crystal surfaces. An important result from our earlier work is that the selectivity of the reaction for the two nitrogen-containing products, N_2 and N_2O , is a strong function of the Rh surface structure¹⁻². On the basis of ancillary data, we suggested that the location of adsorbed NO and N-atoms (formed from dissociation of adsorbed NO) on various Rh surfaces could, perhaps account for the selectivity differences³.

Methods and Materials: Mid- and Far-IRAS measurements were made following low temperature adsorption of NO alone or co-adsorbed with CO on Rh(111) and Rh(110) single crystals.

Results: The first experiments were performed on relatively small ($<1 \text{ cm}^2$) Rh(111) crystals. No reproducible structure in the low-frequency ($200\text{-}700 \text{ cm}^{-1}$) range was observed. A possible reason for this was that a significant fraction of the IR light was not being collected due to the small size of the crystal. A much larger ($\sim 7 \times 3 \text{ cm}$) Rh(110) crystal was procured for a second run in August, 2000. Unfortunately, we were still unsuccessful at obtaining identifiable IR features in the low-frequency region of the spectra. Despite this, we were able to obtain new information concerning the adsorption of NO on these two single crystal surfaces and the effects of co-adsorbed CO by observing changes in the mid-infrared region of the spectra. For example, **Figure 1** shows spectra obtained on Rh(111) following adsorption of 0.5L of NO at 200K. Exposure of this surface to 2L of CO results in the spectra shown at the bottom of the figure. The new peak is, of course, due to chemisorbed CO while the broadening of the features in the NO stretching region of spectra are identical to those observed *in-situ* during high ($\sim 1 \text{ atm.}$) pressure reaction on this single crystal surface. Other data obtained sheds new light on the conditions required to form adsorbed NO-dimers on metal surfaces as well as specific spectral features expected for adsorbed NO_2 .

Conclusions:

- 1) The initial goals of obtaining far-IRAS data in the metal-N stretching region are probably not realizable.
- 2) Broad features in the N-O stretching range are due to effects of CO co-adsorption explaining data obtained *in-situ* during high-pressure reaction.
- 3) Conditions needed for the formation of NO-dimers on metal surfaces were further clarified.
- 4) Spectral features due to adsorbed NO_2 were identified on Rh(110) surfaces.

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References: ¹ C.H.F. Peden, D.N. Belton, and S.J. Schmieg, "Structure Sensitive Selectivity of the NO-CO Reaction over Rh(110) and Rh(111)," *Journal of Catalysis*, 155, 204, 1995; ² G.S. Herman, C.H.F. Peden, S.J. Schmieg, and D.N. Belton, "A Comparison of the NO-CO Reaction over Rh(100), Rh(110) and Rh(111)," *Catalysis Letters*, 62, 131, 1999; ³ Y.-J. Kim, S. Thevuthasan, G.S. Herman, C.H.F. Peden, S.A. Chambers, D.N. Belton, and H. Permana, "Chemisorption Geometry of NO on Rh(111) by X-ray Photoelectron Diffraction," *Surface Science* 359, 269, 1996.

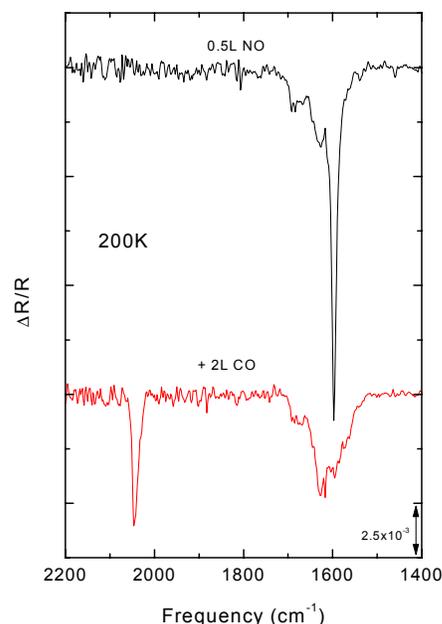


Figure 1. Mid-IRAS data for NO on Rh(111) at 200 K without (top) and with (bottom) co-adsorbed CO.