

**CO and Ethylene Adsorption on Rh Supported on Dysprosium Oxide Thin Films**

D. Mullins (ORNL)

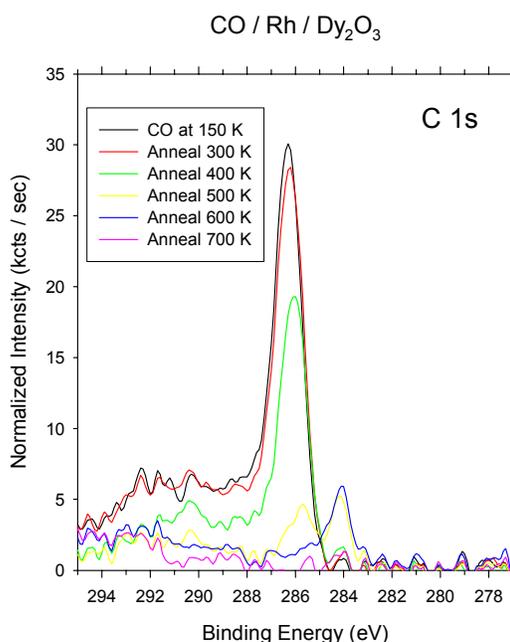
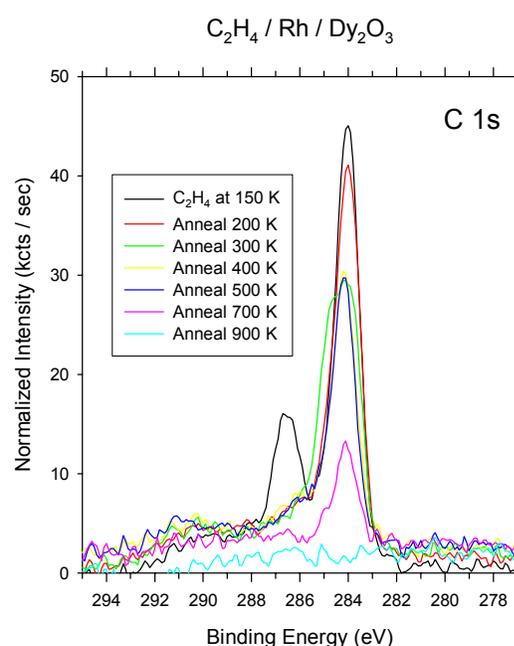
Beamline: U12A

**Introduction:** Cerium oxide has been used as an additive in automotive exhaust catalysts primarily as an oxygen storage medium [1]. UHV experiments on thin films of cerium oxide have shown that when the ceria is reduced to primarily  $\text{Ce}_2\text{O}_3$  it can increase the activity of supported Rh with respect to the dissociation of CO and NO [2].

One possible explanation for this increased dissociation activity is that the O vacancies on the ceria surface provide nucleation sites for forming active Rh islands on the surface. In order to test the influence of O vacancies, we have examined CO and  $\text{C}_2\text{H}_4$  adsorbed on Rh supported on  $\text{Dy}_2\text{O}_3$ .  $\text{Dy}_2\text{O}_3$  has a surface structure similar to reduced ceria but  $\text{Dy}^{3+}$  is not expected to be able to transfer electrons to the Rh as easily as  $\text{Ce}^{3+}$ .

**Methods and Materials:** The  $\text{Dy}_2\text{O}_3$  was deposited by evaporating Dy onto Ru(0001) under an  $\text{O}_2$  pressure of  $10^{-7}$  torr. The Rh was then deposited from a resistive metal source. The CO and  $\text{C}_2\text{H}_4$  were deposited at an exposure sufficient to saturate the first layer ( $\sim 20$  L) at 150 K. The C 1s spectra were recorded using  $\sim 480$  eV excitation. The instrumental resolution was  $< 0.5$  eV.

**Results:** The CO adsorbed molecularly on the Rh as indicated by the C 1s peak at 286.3 eV (Fig. 1). The broad C 1s features between 290 – 294 eV are from carbonate on the  $\text{Dy}_2\text{O}_3$ . Above 300 K the CO starts to desorb as indicated by the decrease in intensity. Above 400 K there is a small amount of decomposition as indicated by the peak at 284.5 eV. The sample is clean at 700 K

Fig. 1 – C 1s spectra for CO on Rh /  $\text{Dy}_2\text{O}_3$ .Fig. 2 – C 1s spectra for  $\text{C}_2\text{H}_4$  on Rh /  $\text{Dy}_2\text{O}_3$ .

Two major peaks are seen following the adsorption of  $\text{C}_2\text{H}_4$  on Rh /  $\text{Dy}_2\text{O}_3$  at 150 K (Fig. 2). The peak near 287 eV is weakly bound  $\text{C}_2\text{H}_4$  on either the oxide or in a multilayer. This peak disappears at 200 K. The other major peak near 284 eV is assigned to  $\text{C}_2\text{H}_4$  on the Rh. This peak broadens toward higher binding energy at 300 K as ethylidyne,  $\text{CCH}_3$  is formed. It then narrows again as the hydrocarbon fragment decomposes into adsorbed C. The most significant feature is that all of the C disappears at 900 K as it reacts with the oxide.

**Conclusions:** The O vacancies on  $\text{Dy}_2\text{O}_3$  do not activate the supported Rh for CO dissociation to a significant degree. C from decomposed  $\text{C}_2\text{H}_4$  reacts with the O from  $\text{Dy}_2\text{O}_3$  even though dysprosia is a “non-reducible” oxide.

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**References:**

[1] *Catalysis by Ceria and Related Materials*, Ed. A. Trovarelli, (Imperial College Press, London, 2002.)

[2] S. H. Overbury and D. R. Mullins in: *Catalysis by Ceria and Related Materials*, Ed. A. Trovarelli, (Imperial College Press, London, 2002) p. 311.