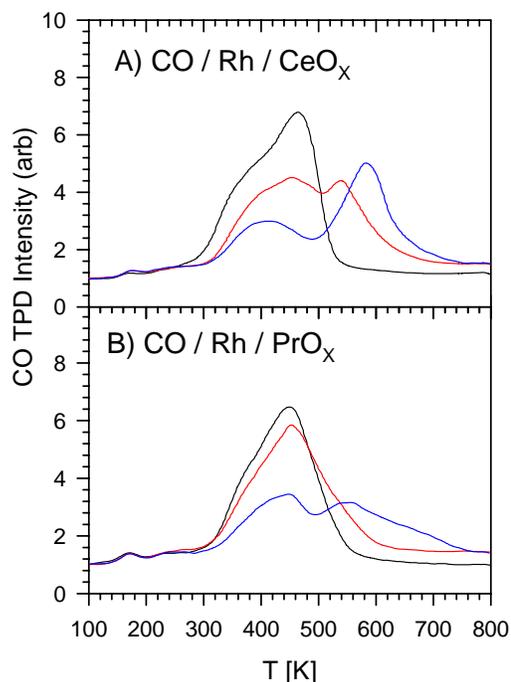


## Comparison of Rh Activity on Praseodymium Oxide and Cerium Oxide Thin Films

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Praseodymium oxide ( $\text{PrO}_x$ ) and cerium oxide ( $\text{CeO}_x$ ) are expected to have similar properties. They have an identical structure and Pr and Ce are both characterized by +3 and +4 oxidation states.  $\text{CeO}_x$  is used extensively in automotive exhaust catalysts as an oxygen storage medium since it readily releases and accepts oxygen as the Ce converts between oxidation states. Now we find that O will readily transport through bulk  $\text{PrO}_x$  and react with a surface reductant. However, in  $\text{PrO}_x$  the O appears to segregate at the surface during reduction whereas the O is uniformly distributed in  $\text{CeO}_x$ .

As a measure of surface reduction, we have examined the dissociation of CO adsorbed on Rh supported on  $\text{CeO}_x$  and  $\text{PrO}_x$ . We have previously demonstrated that when Rh is supported on reduced  $\text{CeO}_x$ , it promotes the dissociation of CO during temperature programmed desorption (TPD). The TPD of CO adsorbed on Rh on (A)  $\text{CeO}_x$  and (B)  $\text{PrO}_x$  is shown in the figure. When the substrates are fully oxidized (black curves) the CO desorption is similar for both oxide supports and is similar to CO desorption from Rh single crystals. This CO desorption below 500 K results from CO that does not dissociate on the Rh particles. Following mild reduction by treating the samples with a small amount of  $\text{C}_2\text{H}_4$  (red curves), the CO adsorbed on the Rh /  $\text{CeO}_x$  surface desorbs in two temperature regions. The CO desorption above 500 K is indicative of CO dissociation on the Rh. This has been confirmed by C XPS that shows the disappearance of CO and the buildup of atomic C above room temperature. The CO from the mildly reduced Rh /  $\text{PrO}_x$  substrate indicates only a slight broadening toward higher temperatures. The C XPS indicates CO dissociation does not occur. We have examined the CO desorption following a wide range of reduction treatments. The Rh /  $\text{CeO}_x$  system demonstrates a continuous variation in CO dissociation that is directly related to the degree of reduction. The blue curve shows that after extensive reduction, more than 70% of the CO dissociates on Rh /  $\text{CeO}_x$ . The CO desorption remains essentially unchanged on Rh /  $\text{PrO}_x$  over a wide range of  $\text{PrO}_x$  reduction. It is only possible to promote CO dissociation on the most highly reduced  $\text{PrO}_x$  (blue curve in B). Only when the thin film substrate is depleted of reducible O, achieving nearly 100%  $\text{Pr}^{3+}$ , is CO induced to dissociate.



These results suggest that the O in  $\text{PrO}_x$  segregates to the surface as the sample is reduced, thereby effectively maintaining the oxygen concentration at the surface and inhibiting CO dissociation. This surface segregation of O may inhibit the re-oxidation of the  $\text{PrO}_x$  bulk. In contrast, ceria appears to disperse the O vacancies uniformly throughout the film making it more effective for O uptake and release and also more effective in altering the Rh activity.