

**Modification of Reaction Properties on Both the Overlayer and the Support:  
Rh Supported on CeO<sub>x</sub> Thin Films**  
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When metals are supported on reducible metal oxides, reaction channels may open up for adsorbed molecules that are not observed when adsorbed on either the metal or the oxide separately. These new channels can take several forms. Molecules on the metal can react directly with the oxide to produce oxidized desorption products. Molecules on the metal may not interact directly with the oxide but may undergo reactions that do not occur in the absence of the oxide. Conversely, molecules adsorbed on the oxide may follow different reaction paths in the presence or absence of metallic nanoparticles.

We have observed reactions occurring on Rh supported on CeO<sub>2</sub> thin films that fall into all of these classes of reaction modifications. Ethylene on Rh single crystal surfaces decomposes to produce gaseous H<sub>2</sub> and atomic C on the Rh surface. Ethylene does not chemisorb on a CeO<sub>2</sub> surface in vacuum. When Rh is supported on ceria, the ethylene sticks to the Rh, decomposes to hydrogen and C and then the C adsorbed on the Rh reacts with the O in the ceria to produce CO.

In an example of the oxide modifying a reaction that occurs on the metal, CO was adsorbed on Rh supported on ceria. In the absence of the oxide, CO adsorbs non-dissociatively on Rh. CO does not chemisorb on the oxide. If the ceria is fully oxidized, CO also adsorbs non-dissociatively on the Rh nanoparticles. However, if the ceria is partially reduced, CO dissociates on the Rh particles producing atomic C that can be observed by core-level photoemission. The atomic C reacts with the O in the ceria to desorb as CO at higher temperatures. The mechanism for the increased dissociation activity is unclear. Structural and electronic modifications have been proposed. However our evidence suggests that the most likely explanation is an interaction at the Rh – CeO<sub>x</sub> interface where CO on the Rh can react with O vacancies in reduced ceria which promotes dissociation.

In a recent series of experiments, methanol was adsorbed on ceria with and without Rh. Methanol is one of the few molecules we have studied that will adsorb and react in vacuum on a fully oxidized ceria surface. CH<sub>3</sub>OH dissociates to produce CH<sub>3</sub>O and OH on the ceria. These surface species react to produce water at low temperatures and formaldehyde at elevated temperatures. This also leads to reduction of the ceria. When Rh particles are present, methanol can react directly with Rh decomposing to H and CO that desorb near 250 K and 460 K, respectively. This is similar to how CH<sub>3</sub>OH interacts with Rh metal and therefore does not show a dramatic metal – support interaction. However, the methoxy that adsorbed on the ceria also decomposes to CO and H<sub>2</sub> rather than CH<sub>2</sub>O. The CO / H<sub>2</sub> desorption temperature is lower than the CH<sub>2</sub>O desorption temperature observed on CeO<sub>2</sub>. These results indicate that a new reaction is occurring at the interface between the Rh and the ceria. Rh promotes the more complete decomposition of CH<sub>3</sub>O at the interface. Since all of the methoxy decomposes through this channel, the chemisorbed species must rapidly diffuse from isolated areas of the oxide to the interface in order to react.

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