

Effect of support oxidation state upon chemisorption and reaction at Rh/ceria model catalysts

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We have studied the chemisorption and thermal evolution of various adsorbates on model catalytic surfaces composed of Rh supported upon highly oriented cerium oxide films. Our principle research focus has been on how the chemistry depends upon the degree of oxidation of the reducible support. First we find that the activity of ceria toward most adsorbates is strongly altered by the degree of reduction. Second, the surface activity of the metal particles is also altered by the extent of reduction of the support. These two factors combine to induce fascinating interactions which control the activity and reaction pathways of the composite system especially during redox reactions in which the extent of oxidation of the support may vary. A detailed understanding of such a model system may clarify the behavior of many catalyst systems for emission control in combustion devices, for example NO/CO conversion and selective reduction of NO under oxidizing conditions.

Cerium oxide films are grown on a Ru(0001) substrate and the extent of oxidation is controlled during growth by varying the oxygen pressure. Ion scattering studies indicate that the ceria is highly oriented to (111) planes of fluoritic CeO₂. Oxygen deficiency is incorporated as anion vacancies leading to increased Ce cations at the surface. Rh is vapor deposited onto oxidized or reduced ceria films. Synchrotron based soft x-ray photoelectron spectroscopy (SXPS) is used to monitor the ceria oxidation state and to identify surface molecular species. TPD is used to monitor evolved molecular species. We have studied adsorption and co-adsorption of NO, N₂O, CO, O₂, H₂O, SO₂, CO₂, H₂ and C₂H₄. We find that generally ceria is difficult to reduce under UHV conditions. Neither CO nor H₂ will easily reduce the ceria films even in the presence of Rh particles. Even H from dissociated water and ethylene evolves primarily as H₂ rather than reducing ceria. Of the species we have studied only C, derived from decomposition of either CO or ethylene, will reduce ceria. On the other hand, NO, O₂, H₂O and SO₂ are very effective in oxidizing reduced ceria.

SXPS permits the ability to distinguish between different molecular and atomic states present on the surface. For example, adsorption and thermal evolution of NO on reduced ceria results in at least seven different states of nitrogen. These can also be distinguished from NO and atomic N on the Rh particles. This ability, coupled with isotopically labeled NO TPD, has been used to monitor the evolution of N species on the composite surface. We find that the oxidation state of the ceria is of crucial importance in defining the reactivity of the supported Rh particles. Dissociation of NO and CO on the small supported Rh particles are both strongly enhanced by reduction of the ceria. Water principally interacts with the reduced ceria support, but its dissociation and subsequent hydroxyl decomposition are enhanced by the presence of Rh. These are clear examples of metal-support effects. Co-adsorption studies of CO and NO suggest that for a reduced ceria support, CO and atomic N react to form isocyanate. At temperatures above 600 K a carbon and nitrogen complex is formed that stabilizes both C and N from reaction to CO and N₂, their ultimate fate. Co-adsorption of ethylene and NO does not yield isocyanate due to the lack of a stable CO species, but the same carbon-nitrogen complex is the most stable surface state.

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.