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Utilizing Metal-Oxide and Oxide-Oxide Interactions for Improved Automotive Emissions Control Catalysts

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Executive Summary

The goal of this research program was to elucidate the structure-activity relationships associated with metal-metal oxide and metal oxide-metal oxide interfaces of relevance in automotive emissions control catalysts. Particular emphasis was placed on explaining the mechanism by which ceria (CeO₂) acts as an oxygen storage medium, oxygen transport on the surface and in the bulk of ceria, and how the ceria-zirconia interaction affects oxygen storage capacity and reactivity. These properties were studied using x-ray surface scattering, pulsed neutron scattering, temperature programmed desorption, x-ray photoelectron spectroscopy and high-resolution electron energy loss spectroscopy.

The overall research program was composed of two primary thrust areas: (1) detailed studies of the lattice and defect structures of ceria and mixed ceria-zirconias, and (2) surface science studies of the reactivity of ceria single crystals and ceria thin films supported on zirconia. A brief overview of the significant contributions made in each of these thrust areas is given below.
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1. Lattice and Defect Structure of Ceria and Ceria-Zirconia

Nano-crystalline ceria, CeO₂, is widely used in automotive three-way catalytic converters. While the majority of the chemical reactions that clean-up exhaust gases take place on metallic catalysts such as Pd and Rh, the addition of ceria significantly enhances the overall performance of the catalytic converter. The primary function of ceria in these catalysts is to dampen out fluctuations in the oxygen partial pressure and maintain the air-to-fuel ratio near the value required for optimal catalyst performance for both CO and hydrocarbon oxidation and NOₓ reduction. This function relies on the fact that ceria has multiple stable oxidation states. Under fuel rich conditions Ce⁴⁺ cations are reduced to Ce³⁺ and release oxygen from the lattice, while under fuel lean conditions this process is reversed. It has been found that mixing ceria with zirconia can enhance the so-called oxygen storage capacity (OSC) of ceria. The mechanism by which the addition of zirconia enhances the OSC is not well understood, but it likely involves the creation and maintenance of oxygen vacancies in the ceria. Understanding the interactions between ceria and zirconia and their influence on crystal structure, defect structures, and transport properties are all critical if one is to achieve further enhancements in the performance of the catalyst. Significant improvement in the catalyst performance is required in order to meet newly enacted emission regulations.

Our project achieved a significant breakthrough by determining the atomistic mechanism of OSC in ceria-zirconia mixtures. Pulsed neutron diffraction experiments carried out at the Argonne National Laboratory revealed the presence of a substantial amount of vacancy-interstitial oxygen defects in nano-crystalline ceria, that appear to be directly tied to the functionality of the material. Thus, maintaining and regenerating these defects is the key to the durability of the system. The neutron results also show that zirconia increases the stability of the defects and keeps ceria slightly reduced, thus facilitating the defect regeneration. In parallel to the pulsed neutron diffraction studies we have also been characterized the reactivity of model CeO₂/ZrO₂ catalysts consisting of ceria thin films supported on zirconia single crystals. The results of these studies have been consistent with the neutron diffraction results. Photoelectron spectroscopy data has revealed that interactions at the ceria-zirconia interface help maintain the ceria film in a slightly reduced state. Ceria films supported on zirconia have also been shown to exhibit significantly different chemical reactivity than ceria films supported on sapphire and bulk ceria. Our results were included in the DOE highlights in 2000, and were prominently mentioned in the review article, “Alternative energy technologies”, by M. S. Dresselhaus and I. L. Thomas IL, Nature 414 (6861): 332-337 NOV 15, 2001.

We then established the direct connection between the amount of defects and the OSC by the parallel measurements of neutron scattering and temperature-programmed-reduction (TPR). It was found that the defect density fell significantly after annealing (aging) at 760°C, while the OSC fell after aging at 800°C, practically at the same aging temperature. The slight difference in temperature reflects difference in the oxygen pressure during aging. By alloying with zirconia, on the other hand, both the defect density and OSC were found to show no change up to about 800°C. We also carried out a series of small angle scattering studies of ceria-zirconia mixture to characterize the degree of nano-domain formation. A part of this work was done as a proprietary project with W. R. Grace, for which W. R. Grace paid all costs.
We have also studied the structure of ultra-thin CeO$_2$ films (a few monolayers) on the single crystal Yttria stabilized cubic ZrO$_2$ substrate, using energy-dispersive surface x-ray scattering technique. We have shown that the ceria films grow epitaxially, but due to the lattice mismatch the grain size is limited to about 80 Å. This study supports our idea of semi-coherent ceria or zirconia rich domains within a single grain. The domains support the integrity of ceria and at the same time the domain boundaries provide easy pathways for oxygen.

Our structural studies have demonstrated the complexity of the local structure of zirconia-doped ceria, and shown how such complexities produce desired effect as ceria nano-particles are used as the oxygen storage media in automotive catalytic converters.

2. Reactivity Studies

Results obtained in this and previous investigations of the reactivity of ceria surfaces have show that oxygen vacancies are the active sites for many reactions involving hydrocarbons and oxygenates. It is difficult, however, to measure the concentration of oxygen vacancies on ceria surfaces. Such information is very important in relating the surface defect concentrations to those in the bulk. In this project, TPD of CH$_3$OH was developed as a chemical probe of oxygen vacancies on ceria surfaces. TPD results obtained from a CeO$_2$(111) single crystal and thin ceria films supported on α-Al$_2$O$_3$(0001) and yttria-stabilized zirconia (100) (YSZ(100)) demonstrated that the reaction of CH$_3$OH on ceria is highly structure sensitive. The presence of surface oxygen vacancy sites and/or exposed surface Ce$^{+3}$ cations has a dramatic effect on reactivity. On nearly stoichiometric surfaces CH$_3$OH adsorbs dissociatively on oxygen vacancy sites to produce surface methoxides. These species undergo oxydehydrogenation to formaldehyde and water at 680 K on CeO$_2$(111) and at 600 to 630 K on CeO$_2$ films supported on YSZ(100) and α-Al$_2$O$_3$(0001). On highly reduced ceria surfaces with exposed Ce$^{+3}$ cations, the primary reaction pathway for adsorbed methoxide intermediates is complete dehydrogenation to CO and H$_2$ which occurs near 670 K. Using this probe of oxygen vacancies it was shown that surfaces of CeO$_2$ films supported on YSZ(100) contain a high concentration of oxygen vacancies and are less thermally stable than either ceria single crystals or ceria films supported on α-Al$_2$O$_3$(0001) and undergo reduction upon heating to only 800 K. Since the reduction of NO$_x$ compounds is an important in automotive catalytic converters the reaction of NO on model Rh/ceria catalysts was also investigated. As was the case with methanol, the adsorption and reaction of NO on ceria was influenced by the oxidation state of the surface cerium cations and the presence of oxygen vacancies. On fully oxidized ceria surfaces NO does not adsorb at 300 K, while on slightly reduced surfaces that have exposed Ce$^{+3}$ cations NO adsorbs molecularly at this temperature. Upon heating to 400 K these molecularly adsorbed species dissociate resulting in oxidation of the surface and the production of gaseous N$_2$. On more highly reduced ceria surfaces, NO dissociates and forms surface nitride species that are stable at temperatures up to 400 K. At higher temperatures the nitrides decompose producing gaseous N$_2$. The reaction of NO on Rh supported on ceria thin film samples was similar to that observed for reaction on Rh/α-Al$_2$O$_3$(0001) and Rh single crystals as long as the surface of the ceria film was fully oxidized. For Rh supported on partially reduced CeO$_2$, 
adsorbed oxygen atoms, formed via dissociation of NO, migrated from the Rh to the ceria resulting in oxidation of the surface of the ceria film. The thermal stability and extent of reduction of the ceria thin films was found to depend on the identity of the underlying support. Ceria films grown on α-Al₂O₃(0001) in 10⁻⁷ torr of O₂ were nearly fully oxidized and appeared to be thermally stable to temperatures in excess of 1000 K. In contrast, ceria films grown on YSZ(100) in 10⁻⁷ torr of O₂ were not fully oxidized again demonstrating that that interactions at the CeO₂-YSZ interface helps maintain the ceria in a slightly reduced state. The YSZ(100)-supported CeO₂ films were also less thermally stable than those on α-Al₂O₃(0001) and became significantly reduced upon heating to temperatures in excess of 750 K.

The results of both the methanol and NO reactivity studies provide a consistent picture of the role of oxygen vacancies on the reactivity of ceria surfaces. The results of these studies are consistent with those obtained in the studies of bulk defect structures in ceria and ceria-zirconia and demonstrate that interactions at the ceria-zirconia interface alter defect concentrations in the ceria and its thermal stability.

Finally, the interaction of SO₂ and other sulfur-containing compounds with ceria was studied during this grant period. Sulfur is known to poison the oxygen storage capacity of ceria; thus understanding how SO₂ reacts on ceria surface is important in developing a model of the deactivation mechanism. XPS and TPD results obtained in this study demonstrated that ceria samples exposed to SO₂ at 298 K are primarily covered with molecularly adsorbed SO₂; however, with oxygen supplied via the ceria to form adsorbed sulfate species also occurs to a small extent at this temperature. Upon heating, molecularly adsorbed SO₂ either desorbs intact or reacts with the ceria to form additional surface sulfates. High concentrations of surface sulfates can be produced by exposing ceria films to mixtures of SO₂ and O₂ at 573 K. Adsorbed sulfates on ceria are stable up to 823 K, and decompose producing gaseous SO₂ and a surface cerium oxy-sulfide upon heating to temperatures between 823 and 1023 K. While sulfate species are known to play a role in the deactivation of the oxygen storage capacity of ceria, the importance of the oxysulfide in deactivation has not previously been considered. In order to determine under what conditions the oxysulfide may play a role in ceria deactivation a series of flow reactor studies with ceria powders was performed in which the sample was exposed to various partial pressure of S₂ and O₂ and the final composition of the ceria was determined. This data was used to determine a Ce-O-S phase diagram for temperatures of relevance to automotive emissions control. The results of this study also clearly demonstrate that formation of cerium oxysulfide plays an important role in sulfur poisoning of the oxygen storage capacity of ceria.

List of Publications Supported by DOE Program #DE-FG02-96ER14682


11. “Reaction of NO on CeO$_2$ and Rh/CeO$_2$ Thin Films Supported on $\alpha$-Al$_2$O$_3$(0001) and YSZ(100)”, R. M. Ferrizz, T. Egami, G. S. Wong, and J. M. Vohs, *Surface Science* 476, 9 (2001).

