A Surface Science Study of Sulfur Dioxide Adsorption on Ceria-Stabilized-Zirconia Model Catalysts

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Stringent environmental regulations of tomorrow present challenges to the current emission control technologies used in many industries. One of the major sources of greenhouse and toxic emissions include automobile exhaust. Automobile manufacturers are one of the industries that are driven to increase the emission control performance in their products. Currently, emission control in automobiles is achieved using devices known as catalytic converters. Catalytic converters are essentially plug-flow-reactors (PFRs) that are packed with some form of a catalytic bed on which the required oxidation and reduction reactions take place at catalytically active sites. The material used to achieve the necessary reduction in activation energy for these reactions to proceed is proprietary in nature, but generally involves the incorporation of a platinum group metal onto the surface or near-subsurface of the catalyst. Normally, this is accomplished by using a ceramic monolith that is dipped into a washcoat that contains the noble metals plus other reaction promoter materials. This thin film of catalytically active material is paramount in reaching the objectives of these devices. A parameter of utmost importance in these materials is the inherent oxygen storage capacity (OSC). OSC plays an important role in the realization of the needed reactions. This is because the catalyst will need to give up available oxygen or take up oxygen from the exhaust as the exhaust cycles in composition due to lean or rich combustion conditions. One of the main problems facing those who design and optimize these systems is the deactivation of the catalyst after a certain time of operation. Certain compounds in automobile exhaust act as poisons and pose a threat to the life cycle of catalytic converters. One of the main deactivating compounds is sulfur dioxide, which is introduced into the exhaust gas from the combustion of small amounts of sulfur species found in most gasoline and diesel fuels. The creation of sulfur tolerant catalytic converters would be highly beneficial for the environment in which we live and poses a technological challenge for those in this area of research. Ultimately, in this research program, the characterization of sulfur dioxide interactions with a $Pd\text{-}CeO_x\text{-}ZrO_y$ model catalyst will be accomplished using techniques that will contribute to this area of research.

The focus of this presentation is on the application of x-ray photoelectron spectroscopy (XPS) surface analysis to a reaction system consisting only of the CSZ promoter material. In order to fully understand the process of deactivation on these catalysts, it is necessary to have an understanding of the interaction, if any, on the individual components before venturing into more complex studies involving multiple components. XPS is an ultra-high-vacuum (UHV) technique with the ability to obtain information on the composition and bonding environment of the atoms in the outermost 50 to 100 angstroms of the material. This highly surface sensitive technique is ideal for this research because the reactions occurring in catalytic converters are essentially occurring on the surface or near the surface of the catalyst washcoat. A specialized reaction cell attached to the main vacuum chamber allows for in-situ exposure of the CSZ promoter materials to reactants and then analysis via XPS without exposing the material to atmospheric conditions. This proves to be highly beneficial in keeping the surface free from contamination. This reaction cell, essentially a gas-solid batch reactor, allows for the variation of exposure pressure and temperature. Reactions will be run using a 5 ppm SO_2, balance N_2 gas feed as the reactant. Exposure pressures up to 1000 torr and temperatures reaching 800 °C will be employed in an attempt to mimic real-world operating conditions experienced by the materials in real catalytic converters. This group of XPS experiments will produce survey and high-resolution spectra that will be analyzed in detail to give meaningful information on the surface sulfur species occurring on these catalyst systems. Preliminary findings have revealed that exposure temperature and pressure play an important role in this adsorption phenomena. In addition, two sulfur species have been identified and their relative ratios compared.