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XANES Studies of Metal-doped CeO₂ Nanoparticles

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Introduction: One of the major efforts of environmental cleanup is focused on controlling the emission of toxic pollutants produced during the combustion of fuels in automotive engines [1]. The so-called three-way catalysts (TWC) are commonly used to reduce the emission of CO, NO_x and hydrocarbons from automobile exhaust [2]. Due to its redox properties, ceria (CeO₂) is a key component in these catalysts [2]. Ceria-supported noble-metal catalysts are capable of storing oxygen under oxidizing condition and release oxygen under reducing conditions via the facile conversion between Ce⁴⁺ and Ce³⁺ oxidation states [3]. To enhance the redox properties and thermal stability of pure ceria, a second metal, often mixed as an additive to form solid solutions with ceria. In this article, we investigate the electronic and chemical properties of metal (Zr, Ca, Tb) doped-CeO₂ nanoparticles

Methods and Materials: Materials under investigations are Ce_{1-x}Zr_xO₂, Ce_{1-x}Ca_xO₂, and Ce_{1-x}Tb_xO₂, which were prepared using an adaptation of the microemulsion method reported previously [4]. Ce L_{III}-edge, Zr L_{III}-edge, Tb L_{III}-edge, and Ca K-edge XANES spectra were collected at the NSLS on beam line X19A in the "fluorescence-yield mode" using a boomerang-type flat crystal monochromator and a special cell with a PIPS detector. The chemical reactivity of Ce_{1-x}Zr_xO₂ towards hydrogen was characterized. Theoretical calculations (DF) were performed to support the experimental results.

Results: For CeO₂ and Ce_{1-x}Zr_xO₂ (x≤5) with particle size between 4 and 7 nm, the atoms in these nanoparticles are arranged in a cubic or pseudo-cubic crystal structure. The lattice constant decreased with increasing Zr content, varying from 5.4019 Å in CeO₂ to 5.3066 Å in Ce_{0.5}Zr_{0.5}O₂. Within the cubic structure, the Zr atoms exhibited structural perturbations that led to different types of Zr-O distances and non-equivalent oxygen atoms in the Ce_{1-x}Zr_xO₂ compounds. Upon the addition of Zr to CeO₂, the Zr positive charge in Ce_{1-x}Zr_xO₂ was smaller than in pure ZrO₂ whereas the Ce positive charge was larger than in pure CeO₂. The variations in cation charge track changes in cation-oxygen distances: the larger the metal-oxygen bond length, the smaller the charge in the cation. The combination of structural (metal-oxygen distance) and electronic (mainly cation charge) effects produced Zr L_{III}-edge XANES spectra with a distinctive line-shape not seen in pure ZrO₂ or CeO₂. The same trend was found when comparing the Ca K-edge spectra of Ce_{1-x}Ca_xO₂ and CaO, or the Tb L_{III}-edge spectra of Ce_{1-x}Tb_xO₂ and Tb_xO. For the reaction of hydrogen with Ce_{1-x}Zr_xO₂, there was a change in the line shape and position of the Ce L_{III}-edge spectra that denotes the formation of Ce³⁺. In contrast, no change was found in the corresponding Zr L_{III}-edge spectra (i.e., no Zr³⁺ production).

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