O 9: Focus Session: Frontiers in Reducible Oxide Surface Science I

Time: Monday 10:30–13:00 Location: HFT-FT 131

Invited Talk O 9.1 Mon 10:30 HFT-FT 131

$\mathbf{CeO_2(111)}$ defect structure, oxygen migration and polaron hopping: A theoretical perspective — •M. Veronica Ganduglia-Pirovano[1], Gustavo E. Murgida[2], Valeria Ferrari[2], Ana Maria Llois[2], Dawei Zhang[3], Zhong-Kang Han[3,4], and Yi Gao[3,4] — [1]ICP-CSIC, Madrid — [2]CAC-CNEA, CONICET, Bs. As. — [3]SINAP-CAS, Shanghai — [4]UCAS, Beijing

Deep understanding of the defect structure of ceria(CeO_2) surfaces is essential to tailor their functionality in applications. For the $CeO_2(111)$ surface, whether surface oxygen vacancies attract or repel, and whether oxygen migration and polaron (Ce^{3+}) hopping are entangled, are heavily debated. Also, a number of surface reconstructions have been observed upon reduction, but their structures have remained elusive. Here, supported by density-functional theory-based modeling, statistical thermodynamics, Monte Carlo and molecular dynamic simulations, and experimental results, we elucidate: (*i*) the subsurface preference at low vacancy concentration and temperature [1,2], (*ii*) the formation of surface vacancy clusters with increased degree of reduction and temperature [2], (*iii*) the nature of the observed $(\sqrt{7}\times\sqrt{7})R19.1^\circ$, $(\sqrt{7}\times 3)R19.1^\circ$, $(\sqrt{3}\times\sqrt{3})$, (3×3), and (4×4) reconstructions [3], as well as (*iv*) the role of Ce^{3+} ions in oxygen vacancy migration [4].

[1] G. E. Murgida, M. V. Ganduglia-Pirovano, Phys. Rev. Lett. 110. 246101 (2013).
[2] Z.-K. Han *et al.*, submitted to Phys. Rev. Materials (2017).
[3] R. Olbrich *et al.* J. Phys. Chem. C, 121, 6844 (2017).
[4] D. Zhang *et al.* in preparation.

Invited Talk O 9.2 Mon 11:00 HFT-FT 131

Interactions at the interface between cerium oxide and metals — •Paola Luches — Istituto Nanoscienze, CNR, Modena, Italy

The interaction between cerium oxide and metals leads to important modifications of the properties of the two materials, which are exploited in many different applications. Surface science studies have largely contributed to the understanding of these interfacial effects at the atomic scale.

I will show the results of our studies of model systems in the form of cerium oxide ultrathin films, focusing on the interplay with Pt in the form of a single crystal (111) oriented substrate. I will discuss the effects of metal proximity in terms of interface charge transfer [1] and atomic exchange. The influence of the metal substrate on the oxide structure and reducibility will also be described [2,3]. In addition, I will present the case in which the metal is in the form of nanoparticles supported on the cerium oxide film surface, discussing the case of Ag in detail [4,5].

I will finally show some promising research directions towards the exploitation of the interaction between cerium oxide and plasmonic metals, aimed at inducing additional functionalities to the composite system.

[1] P. Luches, et al. Adv. Mater. Interfaces 2, 1500375 (2015).
[2] P. Luches, et al. Phys. Chem. Chem. Phys. 16, 18848 (2014).
[3] G. Gasperi, et al. Phys. Chem. Chem. Phys. 18, 20511 (2016).
[4] P. Luches, et al. J. Phys. Chem. C 116, 1122 (2012).
[5] F. Benedetti, et al. J. Phys. Chem. C 119, 6024 (2015).

Invited Talk O 9.3 Mon 11:30 HFT-FT 131

Unraveling surface chemistry Of C-H reforming reactions over Ni-CeOx(111) catalysts — •Sanjaya Senanayake — Brookhaven National Laboratory, Upton, NY 11973, USA

We have utilized a combination of model and powder catalysts composed of Ni and CeOx, employing in situ spectroscopies to elucidate the active state and mechanistic steps associated with C-H bond activation in the ethanol steam reforming (ESR) and Methane Dry Reforming (DRM) reactions. Our results reveal that surface layers of the catalyst substrate can be probed under dynamic reaction conditions using AP-XPS, revealing the surface as highly reduced and hydroxylated under reaction conditions while the small supported Ni nanoparticles are present as Ni0/NixC essential for the C-H conversion processes. In addition, in both reactions, a multifunctional, synergistic role is highlighted in which Ni, CeOx and the interface provide an ensemble effect in the active chemistry that activates C-H (Ethanol/Methane) and leads to H2. We correlate changes to the active phases leading to both C-C and C-H bond cleavage in ESR, and C-H and C-O in DRM but also for carbon accumulation or coking that are intrinsic properties of such reactions. The interface (Ni-ceria) facilitates the C-C bond breaking step while the pathways that lead to H2 production may occur from the recombination of OH and CHx species. Additionally, we discuss important insights into the stability and selectivity of the catalyst in the presence of co-reactants and the strategies that will help correlate improved catalyst design for selective bond breaking and forming processes.

O 9.4 Mon 12:00 HFT-FT 131

Progressive reduction from $\mathbf{CeO_2}$ to $\mathbf{Ce_2O_3}$ — •Reinhard Olbrich[1], Gustavo E. Murgida[2,3], Valeria Ferrari[2,3], Clemens Barth[4], Ana M. Llois[2,3], Michael Reichling[1], and M. Veronica Ganduglia-Pirovano[5] — [1]Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany — [2]Departamento de Física de la Materia Condensada, GIyA, CAC-CNEA, 1650 San Martín, Buenos Aires, Argentina — [3]Consejo Nacional de Investigaciones Científicas y Técnicas - CONICET, C1033AAJ, Buenos Aires, Argentina — [4]Aix-Marseille University, CNRS, CINaM UMR 7325, 13288 Marseille, France — [5]Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas- CSIC, 28049 Madrid, Spain

The progressive reduction from CeO_2 to Ce_2O_3 of a 180nm thick ceria film annealed in an ultra-high vacuum (UHV) environment at temperatures up to 1100 K is observed by direct imaging with a non-contact atomic force microscope (NC-AFM). By combining high-resolution NC-AFM imaging with spin-polarized DFT+U calculations, we identify four surface reconstructions namely $\sqrt{(7)}\times\sqrt{(7)}$R19.1° Ce_7O_{12}, $\sqrt{(7)}\times 3$R19.1° Ce_3O_5, $\sqrt{(3)}\times\sqrt{(3)}$R30° Ce_3O_5 and 1 × 1 Ce_2O_3. We combine DFT total energy calculations with statistical thermodynamics to explain the sequence of occurrence of the observed phases and their coexisting at evaluated temperatures. The $\sqrt{(7)}\times 3$ phase is the only phase that has an unexpected oblique rather than a hexagonal structure. This phase only exists as a thin reduced over layer and can not be prepared in the bulk.

O 9.5 Mon 12:15 HFT-FT 131

Covalent versus localized nature of 4f electrons in ceria — •Tomáš Duchoň[1], Marie Aulická[1], Eike F. Schwier[2], Hideaki Iwasawa[2], Chuanlin Zhao[3], Ye Xu[3], Kateřina Veltruská[1], Kenya Shimada[2], and Vladimír Matolín[1] — [1]Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 18000 Prague 8, Czech Republic — [2]Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima, Hiroshima 839-0046, Japan — [3]Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803, USA

4f electrons play an important role in the redox cycle of rare earth oxides. Here, we utilize isostructural transition between CeO2(111) and c-Ce2O3(111) to reveal the nature of 4f contribution in the valence band of cerium oxide. Separating intra- and interatomic photoemission processes via combined resonant angle-resolved photoemission spectroscopy and density functional theory investigation, we report on c-f hybridization and its modification through anion doping as a viable means of steering the surface chemistry of cerium oxide.

O 9.6 Mon 12:30 HFT-FT 131

Surface structure and reactivity of cerium oxide — •Chengwu Yang, Alexei Nefedov, Yuemin Wang, and Christof Wöll — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany.

Ceria is becoming a ubiquitous constituent in catalytic systems for a variety of applications over the last forty years. The high catalytic activity is connected with its strong redox properties making ceria the ideal buffer system for oxygen in a catalytic process. The importance of this material has triggered numerous experimental and theoretical studies. The studies on bulk single crystal surfaces, however, are still scarce.

On a novel UHV-FTIRS we used carbon monoxide (CO) as probe molecule to detect the surface structure of ceria bulk single crystals and nanocrystals. Our results indicate that CO is capable of probing surface oxygen vacancies and distinguishing facet orientations. After the determination of ceria surface structure, the unexpected origin of photoreactivity of ceria has been investigated by monitoring the UV-induced decomposition of nitrous oxide (N2O) on well-defined single crystals of ceria. We demonstrate that ceria becomes photoactive only in the presence of surface O-vacancies with largely undercoordinated electron-rich Ce3+ cations. Additionally, we also provide direct spectroscopic evidence for the formation of active dioxygen species (superoxo and peroxo species) on the reduced ceria (110) and (100) surfaces upon oxygen (O2) adsorption. However, neither of these species was present on ceria (111).

O 9.7 Mon 12:45 HFT-FT 131

Spectroscopic evidence for the controlled formation of catalytically active Pt nanoparticles supported on ceria — •Junjun Wang, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344, Eggenstein-Leopoldshafen, Germany

Ceria-supported Pt catalysts have received increased attention from both fundamental and technological perspectives due to their applications in several fields such as automotive exhaust cleaning and hydrocarbon reforming. It has been proposed that the catalytic activity and utilization efficiency of Pt can be significantly enhanced by decreasing the particle size to ultrafine clusters. In the present work, the surface structure and oxidation states of ceria-supported Pt nanoparticles under alternating reductive and oxidative conditions were monitored by ultrahigh vacuum IR spectroscopy using CO as a probe molecule. Our results provided direct spectroscopic evidence for the re-dispersion of Pt particles in ceria after oxidation at moderate temperatures. It was found that the subsequent reduction treatments at different temperatures lead to a controlled formation of ultrafine Pt particles. The combined IR and high-resolution XPS data allowed us to gain detailed insights into the strong Pt-ceria interaction and the dynamic behavior of Pt clusters under reductive and oxidative atmospheres.