On Alkyne Hydrogenation Reactions on Ceria:

Model Studies on CeO_2(111) Films

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Ceria (CeO_2) was recently identified as a promising catalyst in the selective hydrogenation of alkynes to alkenes.[1] This reaction occurs primarily on highly dispersed metal catalysts, such as Pd, but rarely on oxide surfaces. The origin of the outstanding activity and selectivity observed on CeO_2 remains unclear. We show that one key aspect of the hydrogenation reaction – the interaction of H_2 with the oxide – depends strongly on the presence of O vacancies within CeO_2. Using infrared reflection absorption spectroscopy (IRAS) on well-ordered CeO_2(111) thin films and density functional theory (DFT) calculations, we show that the preferred heterolytic dissociation of molecular hydrogen on CeO_2(111) requires H_2 pressures in the mbar regime. Hydrogen depth profiles measured by nuclear reaction analysis (NRA) indicate that H species stay on the surface of stoichiometric CeO_2(111) films, whereas H may be incorporated into the bulk of partially reduced CeO_{2-x}(111) films (x~0.2). Complementary DFT calculations suggest that oxygen vacancies facilitate H incorporation below the surface and that they may be the key to the stabilization of hydridic H species in the ceria bulk.[2] Gas chromatography (GC) studies on the reactivity of the stoichiometric and reduced ceria films are under way.

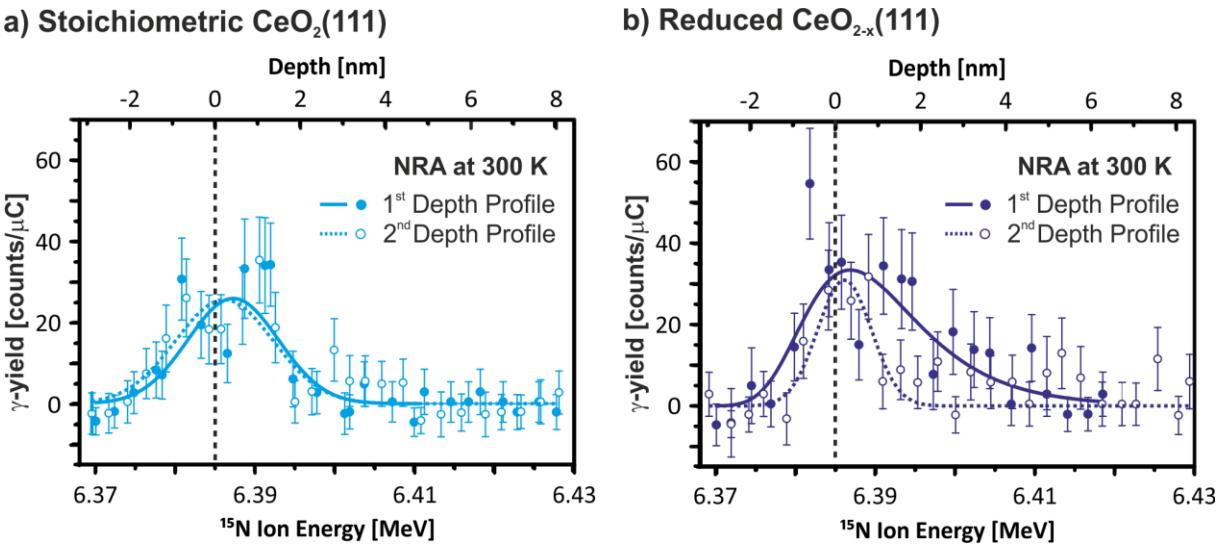

Figure 1: NRA H depth profiles of stoichiometric CeO_2(111) and partially reduced CeO_{2-x}(111) recorded at 300 K after treatment with 10 mbar H_2. Surface H species are found on CeO_2(111), whereas CeO_{2-x}(111) also incorporates semistable H species into its bulk. [1]

References:
[1] Vilé, G.; Bridier, B.; Wichert, J.; Pérez-Ramírez, J. *Angew. Chem. Int. Ed.* ***51***, 8620 (2012).
[2] K. Werner, X. Weng, F. Calaza, M. Sterrer, T. Kropp, J. Paier, J. Sauer, M. Wilde, K. Fukutani, S. Shaikhutdinov, H.-J. Freund, *J. Am. Chem. Soc.,* **139** (48), 17608 (2017).