

Hydrogen in oxides by resonant photoemission

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Oxides are crucial materials in catalysis, e.g., used as support materials promoting hydrogenation reactions via spillover [1]. Since long, there is debate how and to what extent the reducibility of a support influences catalysis [2]. This asks for thorough investigation of the interaction of hydrogen with the oxide and the corresponding changes of the electronic structure. The measurement of hydrogen induced changes on the electronic structure of transition metal oxides by X-ray photoelectron spectroscopy is a challenging endeavour due to the required severe vacuum conditions, and since the origin of the photoelectron cannot be unambiguously assigned to hydrogen. Using a membrane approach to X-ray photoelectron spectroscopy, in combination with tuneable synchrotron radiation we measure simultaneously core levels and valence band up to a hydrogen pressure of 1000 mbar. We discuss two archetypal systems: mildly reducible TiO₂, in which defects are induced by hydrogenation, and NiO, which is eventually reduced to the element and water. In TiO₂, defect states are formed, which we associate to shallow hydrogen states at mild conditions ($T \sim 400\text{K}$, $p \sim 1\text{ bar}$) as no additional changes of the valence bands are observed. At slightly higher temperatures ($T \sim 500\text{ K}$, $p \sim 10^{-9}\text{ bar}$) new states occur on expense of the shallow states. With the occurrence of these states, the valence band structure changes indicative of oxygen - titanium bond breaking, and is thus associated with oxygen deficient defect states. In resonant conditions, electrons are excited to the conduction band and are then either trapped by specific defect states, or are annihilated via recombination by others [3]. The correlation of the results from resonant and non-resonant photoemission reveals that shallow hydrogen induced defects serve as trap centers, while defects associated with oxygen-titanium bond breaking serve as recombination centers suppressing trap state emission. In NiO, hydrogenation removes the naturally present oxygen excess defects (Ni-deficient states). These stoichiometric defects are interpreted as the precursor of metallic Ni, which are eventually formed at higher temperatures as observed by our measurements. Although oxygen deficient states are likely formed during the course of reaction, the ability of the stoichiometric defects to split hydrogen [4] and thereby catalyse the phase transformation towards metallic nickel exceeds that of oxygen deficient states. The observations explain the peculiar reduction phase transformation of NiO.

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