

Electronic processes at the surface of ceria-based materials during H₂O chemisorption

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The chemisorption of H₂O on the surface of ceria (CeO₂) is at the basis of several important catalytic reactions. Cerium oxide behaves as a semiconductor surface. Chemisorption on semiconductor surfaces alters the charge potential on the surface which, in turn, influences the chemisorption capacity of the surface (as well as bulk properties such as the electrical conductivity and the thermoelectric workfunction).

The objective of the presented study is to relate the adsorption characteristics of different ceria-based materials to the band structure of the materials. In addition, to understand the physical processes underlying the effect of intrinsic and extrinsic defects on the chemisorptive capacity. To do so, adsorption isotherms for nanoparticles of ceria, oxidized and partially reduced, as well as ceria doped by dopants of different types (acting as acceptor as Gd or donor as U) were recorded at room temperature. Concurrently, the heats of adsorption were determined calorimetrically as a function of coverage. The adsorption isotherms were analyzed in view of the electronic theory of chemisorption on semiconductor surfaces. The form of the isotherm does not follow that of classical isotherms (such as Langmuir) which do not explicitly take into account the electronic behavior of the surface. Rather, it follows more complex expressions which account for the band structure of the specific system under consideration. The analysis leads to the determination of the variation of the surface potential with increasing H₂O coverage in the different ceria based samples.

The results provide new insight on the complex interaction between H₂O adsorbates and the surface of ceria and on the influence of foreign atoms on this interaction.