The Role of Surface Hydroxyls in the Entropy-Driven Adsorption and Spillover of H_2 on Au/TiO_2 Catalysts

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Hydrogen spillover involves the migration of H atom equivalents from metal nanoparticles to a metal oxide support. This phenomenon is well documented, bridging heterogeneous catalysis, semiconductor surface chemistry, and photo-/electro-catalytic hydrogen evolution. It has broad technological impacts for H_2 production, utilization, and storage as well as in catalysis. Spillover has been reported for many materials including single atom alloys, high entropy alloys, metal-organic frameworks, and metal-semiconductor photoelectrodes. While well documented, H spillover is still a poorly understood and largely unquantified phenomenon. Here we show weak, reversible H_2 adsorption on Au/TiO_2 catalysts, is due to spillover onto the support and report the first adsorption isotherms for H spillover (H*). Using in-situ Fourier-transform infrared spectroscopy coupled with volumetric H_2 chemisorption, we are able to extract the H* surface concentration and the associated adsorption energetics as a function of temperature and pressure. The spillover species is best described as a loosely coupled proton/electron pair distributed across the titania surface hydroxyls. In stark contrast to traditional gas adsorption systems, H* adsorption increases with temperature. This unexpected adsorption behavior has two origins. First, entropically favorable adsorption results from high proton mobility and configurational surface entropy. Second, the number of spillover sites increases with temperature, due to increasing hydroxyl Bronsted acid–base equilibrium constants. Increased H* adsorption correlates with the associated changes in titania surface zwitterion concentration. This study provides a quantitative assessment of how hydroxyl surface chemistry impacts spillover thermodynamics and contributes to the general understanding of spillover phenomena.