

Mechanism of the Water-Gas Shift Reaction at the Metal-Oxide Interface: Insights from First Principles Calculations

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The traditional approach to the optimization of metal/oxide catalysts has focused on the properties of the metal and the selection of the proper oxide for its dispersion. The importance of metal–oxide interfaces has long been recognized, but the molecular determination of their properties and role is only now emerging. In this talk we focus on the water gas shift reaction, WGS, a chemical process that allows for obtaining clean molecular hydrogen: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. Bulk like phases or extended surfaces of coinage metals show low catalytic activity that improves when supported on a metal-oxide. Multiple reaction mechanisms have been proposed. In the redox mechanism, CO reacts with oxygen derived from the dissociation of H_2O . In the associative process, the formation of a carbonaceous CO_xH_y intermediate must precede the production of H_2 and CO_2 . The mechanism involves several steps that can take place at different sites of the catalyst: the metal, the support or the interface. Besides the dispersion effect, the role of the support is to increase the interaction with water and facilitate its dissociation. DF calculations show that supported CeO_x nanoparticles (NPs) are highly efficient in water splitting (Fig 1, left). Furthermore The $\text{M}/\text{CeO}_x/\text{TiO}_2$ (110) surfaces display outstanding activity for the WGS, in the sequence: $\text{Pt} > \text{Cu} > \text{Au}$ (Fig 1, right). Such a high catalytic activity reflects the unique properties of the mixed-metal oxide at the nanometer level. STM and DF calculations show that Ce deposition on TiO_2 (110) at low coverage gives rise to Ce_2O_3 dimers specifically aligned, indicating that the substrate imposes on the ceria NPs unusual coordination modes enhancing their chemical reactivity.

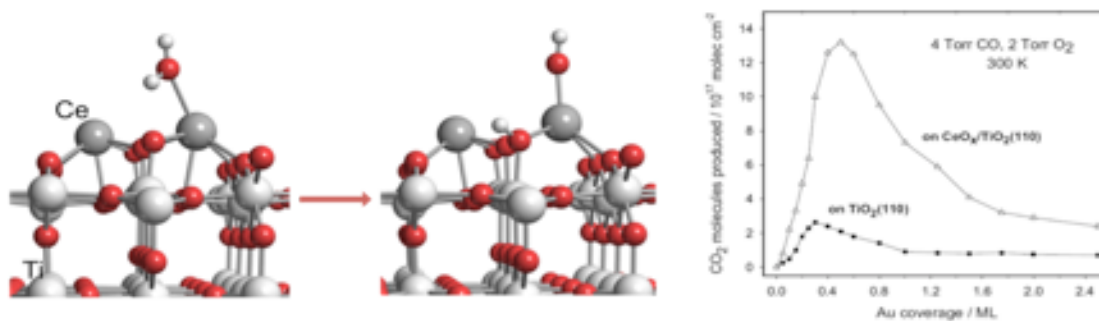


Fig. 1. Left: water dissociation on $\text{CeO}_x/\text{TiO}_2(110)$. The process is exothermic by 0.70 eV and the activation barrier is of only 0.04 eV. Right: catalytic activity of gold NPs supported on $\text{TiO}_2(110)$ and $\text{CeO}_x/\text{TiO}_2(110)$.

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