Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption and Kinetics at Surface versus Subsurface

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Abstract: Transition metals are commonly used to catalyze transformations of small organic compounds, but the mechanisms of these catalytic reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. Does subsurface oxygen affect catalysis by changing the electronic and geometric properties of silver, or does it emerge to the surface to directly interact with reactants? Does it initiate or promote surface reconstructions of silver? Does the participation of subsurface oxygen change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage? Answers to such questions will promote a deeper mechanistic understanding of heterogeneous catalysis by silver, and help to design more effective industrial catalysts. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces, and examine their effects on the structural and catalytic properties of silver. On the Ag(111) surface, it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption, resulting in oxygen binding more strongly to the subsurface than to the surface at coverages above 0.5 ML. In contrast, surface adsorption remained stronger than subsurface adsorption at higher coverages on the Ag(110) surface. Calculations also show that kinetic barriers for formation of subsurface oxygen or its emergence into the surface are strongly dependent on coverage, indicating that the direct participation of subsurface oxygen in catalysis might strongly depend on coverage. Overall, our results provide valuable insight into the competition between adsorption and kinetics of oxygen on different facets of the silver surface, the importance of charge transfer in the binding and motion of atomic oxygen on silver, and the role of subsurface oxygen in catalysis by silver.