165c Co Oxidation by High-Concentration Oxygen Phases on Pt(111)

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A variety of surface oxygen states or phases can be present on Pt catalysts at the high pressures typically employed in commercial catalysis. However, due to the low reactivity of O_2 toward noble metals, it is challenging to prepare and characterize high coverage oxygen phases on Pt surfaces under well-controlled ultrahigh vacuum (UHV) conditions. We have employed an atomic oxygen beam to generate high-coverage oxygen phases on Pt(111) in UHV, and characterized the reactivity of these phases toward the oxidation of CO using temperature programmed reaction spectroscopy (TPRS) and direct, isothermal rate measurements. The TPRS results show that the saturation coverage of CO is approximately the same for different phases of chemisorbed oxygen atoms, but that the reactivity is slightly enhanced in phases with higher oxygen concentrations. In contrast, CO uptake is immeasurable when the surface is covered with Pt oxide and held at 100 K, indicating that CO binds very weakly on the oxide. At constant surface temperatures between 300 and 500 K, the CO_2 production rate exhibits an initial jump upon exposing the surface to a CO molecular beam, followed by a slow, linear increase toward a maximum, with this induction period increasing as the initial coverage of chemisorbed oxygen atoms increases. Significantly longer induction periods are observed for CO oxidation on oxide-covered Pt(111). The key characteristics of the CO oxidation kinetics are well reproduced by a model in which CO chemisorbs via a weakly bound precursor state on oxygen-covered regions of the surface, and reacts uniformly within domains of chemisorbed oxygen. For surfaces partially covered with Pt oxide, the observed rate behavior is consistent with CO adsorption exclusively on surface regions containing chemisorbed oxygen atoms, and CO oxidation occurring only within these domains and at the edges of oxide particles. These results show that CO adsorption and binding play a dominant role in determining the CO oxidation kinetics on various high-coverage oxygen phases on Pt(111).