Probing the mechanism of facile water dissociation on oxygen covered Cu(111) by Reflection Absorption Infrared Spectroscopy (RAIRS)

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The presence of oxygen atoms on a Cu(111) surface strongly reduces the activation barrier for water dissociation, as compared to bare Cu(111). In this work, we present a direct experimental observation of the hydrogen abstraction mechanism for H_2O dissociation on a O/Cu(111) surface using reflection absorption infrared spectroscopy (RAIRS). By dosing $^{18}O_2$(g) onto a Cu(111) single crystal, we create a partially oxidized ^{18}O/Cu(111) surface, which is subsequently exposed to a flux of $H_2{}^{16}O$ molecules, resulting in the detection of two RAIRS peaks assigned to ^{18}OH(ads) and ^{16}OH(ads). With continued $H_2{}^{16}O$ exposure, the ^{18}OH(ads) RAIRS signal decreases rapidly while the ^{16}OH(ads) signal continues to increase, indicating a disproportionation reaction of the adsorbed hydroxyl species, resulting in net desorption of $H_2{}^{18}O$(g) and replacement of ^{18}O(ads) by ^{16}O(ads).

