Coverage-dependent Adsorption and Reactivity of Formic Acid on $Fe_3O_4(001)$

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Formic acid (FA) is a crucial intermediate in important catalytic reactions such as Fischer-Tropsch synthesis and water-gas shift. On oxide surfaces, FA generally undergoes decomposition to CO or CO_2 through decarbonylation or decarboxylation mechanisms. We study the adsorption of FA on the reconstructed $Fe_3O_4(001)$ surface, followed by stepwise annealing using a combination of scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy, low-energy electron diffraction, and temperature programmed desorption (TPD). Dissociative adsorption of formic acid leads to the adsorbed formate and hydroxyl species on the surface. At low coverages, isolated formates and hydroxyls are observed. At intermediate coverages, local clustering of formate is observed, giving rise to both (1×1) and (2×1) surface periodicities. A fully saturated surface shows formates arranging predominately in the (1×1) periodicity but retains some formates in the (2×1) periodicity in agreement with prior studies.[1] Annealing the surface to 450 K induces the formation of a well-ordered surface with a (1×1) periodicity, which results in the lifting of the surface reconstruction. Stepwise annealing enables monitoring of formate reactivity and surface structure changes. Two major peaks are observed via TPD at 525 and 565 K, indicating that the formate undergoes decarbonylation to CO and H_2O, with decarboxylation to CO_2 as a minor reaction pathway. STM reveals that annealing to 550 K leads to a partial recovery of the surface reconstruction and a possible formation of single oxygen vacancy defects. Further annealing to 650 K, which leads to the conversion of all formate species, reveals the formation of pits extended along the Fe rows. This is consistent with the non-stoichiometric formic acid decarboxylation accompanied by water formation proceeding via the Mars van Krevelen mechanism. We are currently focusing on understanding the initial stages of pit formation and the role of hydroxyls in reaction mechanisms. This work underscores the significance of fundamental studies to unravel the effect of structural changes on reaction mechanisms and dynamics.

1. Gamba, O., et al. (2015). "Adsorption of formic acid on the $Fe_3O_4(001)$ surface." The Journal of Physical Chemistry C **119**(35): 20459-20465.