

Heterogeneous adsorption and local ordering of formic acid on a magnetite surface

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Magnetite (Fe_3O_4) is an important and diverse transition metal oxide with applications as a catalyst in various industrial processes such as the water-gas shift reaction [1] and the Fischer-Tropsch synthesis [2]. Formic acid (HCOOH), as the elementary carboxylic acid, is proposed to occur as an intermediate during these reactions. In material science magnetite nanoparticles are linked by larger carboxylic acids to form supercrystals with exceptional mechanical properties [3]. Thus, a detailed atomic understanding of the interaction at the magnetite surface/carboxylic acid interface is vital. In this contribution the adsorption of formic acid on the magnetite (111) single crystal surface is studied under UHV conditions at room temperature. Our FT-IRRA spectroscopy results and DFT calculations show dissociative adsorption of formic acid in quasi-bidentate and chelating geometries, the latter being stabilized by the presence of tetrahedral iron vacancies at the surface [4]. The locally observed $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure by STM consists of formate in a triangular arrangement, adsorbed predominantly in chelating geometry. Furthermore, differences to the adsorption of formic acid on magnetite (001), where only a bidentate-bridging adsorption mode occurs [5,6], are discussed.

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