Carbon−Carbon Bond Formation on Model Titanium Oxide Surfaces: Identification of Surface Reaction Intermediates by High-Resolution Electron Energy Loss Spectroscopy

Hengshan Qiu, Hicham Idriss,† Yuemin Wang,* and Christof Wöll

Physical Chemistry I, Ruhr-University Bochum, 44780 Bochum, Germany

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The interaction of CH_2O with perfect and defective $TiO_2(110)$ surfaces (produced by overannealing and Ar ion sputtering methods) was studied by thermal desorption spectroscopy, high-resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) calculations. Exposing the perfect $TiO_2(110)$ surface to CH_2O at 100 K leads to the formation of physisorbed CH_2O and to polymerization of CH_2O, yielding paraformaldehyde. The latter is bound to the 5-fold coordinated surface Ti atoms and is found to decompose and release CH_2O at about 270 K. On the defective $TiO_2(110)$ surface, CH_2O adsorbs more strongly on oxygen vacancy sites, ultimately forming a diolate ($-OCH_2CH_2O-$) species, as demonstrated by HREELS. The assignment of the vibrational frequencies was aided by theoretical calculations on the DFT-B3LYP level. Upon heating to higher temperatures, this species undergoes deoxygenation, resulting in ethylene formation.