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

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The interaction of CH₂O with perfect and defective TiO₂(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 TiO₂(110) surface to CH₂O at 100 K leads to the formation of physisorbed CH₂O and to polymerization of CH₂O, yielding paraformaldehyde. The latter is bound to the 5-fold coordinated surface Ti atoms and is found to decompose and release CH₂O at about 270 K. On the defective TiO₂(110) surface, CH₂O adsorbs more strongly on oxygen vacancy sites, ultimately forming a diolate (−OCH₂CH₂O−) 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.

1. Introduction

Chemical reactions occurring on surfaces of titanium oxide have been studied in great detail, and many specific information regarding atomic arrangement, electronic states, surface relaxation, and point defects such as “oxygen vacancies” are now available. The most studied surface of rutile TiO₂ is the (110) surface that contains alternating rows of 5-fold coordinated Ti atoms (Ti₅c) and 2-fold coordinated bridging O atoms (O₂c). This surface is generally regarded as a prototype model for rutile TiO₂. This surface however, no matter how carefully prepared, contains oxygen vacancies in ultrahigh vacuum (UHV), with their density depending on the surface annealing temperature and oxygen partial pressure. A large fraction of these oxygen vacancies can be healed by water dissociation yielding two surface hydroxyls per one surface oxygen vacancy. Many catalytic reactions rely on the dynamic equilibrium between the addition and removal of oxygen atoms on the surface. For example, CO oxidation in a Mars Van Krevelen type on RuO₂(110) surfaces as well as oxidative dehydrogenation of alcohols and hydrocarbons all rely on the dynamics between surface oxygen vacancies and gas phase oxygen pressure. In surface science, for most of these oxidation/reduction processes the decomposition (dissociation) pathways are studied where the number of moles consumed is equal or less to the number of moles produced. This preference is in part due to what it generally referred to as the pressure gap; simply stated as high-vacuum favoring dissociation and high-pressure favoring association. However, some counter examples are persistent in surface reactions where surface−adsorbate interactions lead to building up of large molecules via carbon−carbon, carbon−oxygen, and carbon−nitrogen bond formation. These coupling reactions are among the most essential chemical reactions in nature.

In UHV, carbon−carbon bond formation was reported on O-defected TiO₂ and UO₂ single crystals. Oxidative coupling of acetylene to furan was also detected on a Pd(111) single crystal surface.

Organometallic and organic chemists recognized early on that Ti compounds are active for coupling reactions of carbonyl compounds via carbon−carbon bond formation. During this catalytic process Ti atoms are oxidized, ultimately to Ti⁴⁺, a reaction termed the McMurry reaction. Orbital symmetry is given as the reason for the high activity of the surface Ti species, although detailed studies are not reported. It is also worth mentioning that this reaction is not observed on many other transition metals, and of all the transition metals investigated, Ti is the most active. The reductive coupling of carbonyls on reduced TiO₂(001) single crystals was studied by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The results indicated that a diolate type species (−OCH₂CH₂O−) is most likely formed as an intermediate between the carbonyl (R(R′)=O) and the symmetric hydrocarbon (R(R′)=C=C(R′)) as well as that of carboxyls (ca. 285 eV) and of carboxyls (ca. 288 eV). However, photoelectron spectroscopy provides indirect evidence of the surface species formed during the reaction. No unambiguous evidence for the formation of a diolate species on TiO₂ single crystal surfaces has been reported.

High resolution electron energy loss spectroscopy (HREELS) has been extensively used to characterize adsorbed species on metal single crystal surfaces (see, e.g., refs 27–32). In contrast to metals, the application of this technique to oxide surfaces is rather scarce. This lack of information is to a large extent due to the intense Fuchs−Kliewer phonon losses that make the adsorbate-related losses very difficult to detect. Two methods to overcome this problem have been proposed in the literature: Fourier deconvolution of combination losses and collection of spectra under conditions where impact scattering is enhanced. More recently, using a combination of both methods, high-quality HREELS data have been reported for different adsorbates on ZnO and TiO₂ surfaces. The successful application of HREELS to oxides and the advanced understanding of the surface structure of TiO₂(110)