Direct Observation of C₂ Hydrocarbon–Oxygen Complexes on Ag(110) with a Variable-Low-Temperature Scanning Tunneling Microscope

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A variable-low-temperature scanning tunneling microscope (STM) was used to observe oxygen (O₂), ethylene (C₂H₄), and acetylene (C₂H₂) molecules on a Ag(110) surface and the various complexes that were formed between these two hydrocarbons and oxygen at 13 K. Ethylene molecule(s) were moved to the vicinity of O₂ either by STM tunneling electrons at 13 K or thermally at 45 K to form (C₂H₄)ₓ−O₂ (x = 1–4) complexes stabilized by C−H•••O hydrogen bonding. Acetylene−oxygen complexes involving one or two acetylene molecules were observed.

The heterogeneous selective oxidation of hydrocarbons is a topic of enormous industrial importance and has therefore been extensively studied. Most thermodynamically favorable hydrocarbon oxidation reactions give rise to undesirable products such as CO₂ and H₂O;¹⁻³ hence, achieving acceptable selectivity in hydrocarbon oxidation is particularly important in industrial processes. Selectivity with respect to the formation of useful partial oxide (intermediates) can only be accomplished via kinetic control; however, such control requires a good understanding of the surface reaction mechanisms.¹⁻⁴ Most previous studies of hydrocarbon oxidation have been performed at silver surfaces because silver-catalyzed partial oxidation of hydrocarbons, in particular, epoxidation (ethylene to ethylene oxide), is the most widely exploited catalytic oxidation reaction on an industrial scale.⁵ Achieving a molecular level understanding of the epoxidation mechanism is arguably the most important challenge in this field.⁶⁻¹⁰ Thus, to enhance the basic knowledge on hydrocarbon catalytic oxidation reactions, we carried out molecular scale imaging of the complexes formed between an oxygen molecule and C₂ hydrocarbons (ethylene or acetylene) on the silver surface using a scanning tunneling microscope.

An interesting aspect of hydrocarbon oxidation is its uniqueness: not only is silver the only metal that catalyzes the epoxidation reaction but also ethylene is the only hydrocarbon that is epoxidized with high selectivity (up to 80%).¹¹,¹² Olefins such as propylene,¹¹,¹³ styrene,¹⁴ 3,3-dimethylbutene,¹⁵ norborne,¹⁶ and butadiene are also epoxidized on a silver surface but with very low selectivities (below 5%).¹¹,¹³ Other molecules such as butenes and pentenes are mainly combusted into CO₂ and H₂O.¹⁷ Alkynes (acetylene and propyne) also undergo complete oxidation; no epoxides have been observed to form on a silver surface.¹⁸,¹⁹ In addition, the identity of the adsorbed oxygen species responsible for the ethylene epoxidation and combustion has been the subject of a long-standing controversy. Three mechanisms have been put forward for epoxidation at a silver surface, involving surface molecular oxygen,²⁰⁻²² atomic oxygen,²⁴⁻²⁸ and subsurface oxygen²⁸ as the active species. Thus, three main factors appear to affect the mechanism by which hydrocarbons are oxidized at metal surfaces: the metal used, the structure of the hydrocarbon, and the identity of oxygen species. Despite numerous reports on the epoxidation on silver, an understanding of the complete reaction pathway is still required.

In this paper, we present scanning tunneling microscopy (STM) images of hydrocarbon−O₂ complexes formed on Ag(110) after one or more ethylene or acetylene molecules had been manipulated into the vicinity of an oxygen molecule on the silver surface either with tunneling electrons (at 13 K) or thermally (at 45 K). Elucidation of the characteristics of these complexes may provide insights into the fundamental mechanisms of hydrocarbon chemistry.

Experiments were performed using a homemade, variable-temperature STM,²⁹ housed inside an ultrahigh vacuum chamber with a base pressure of 2 × 10⁻¹¹ Torr (2.7 × 10⁻⁹ Pa). The Ag(110) sample was prepared by 500 eV neon ion sputtering followed by annealing at 693 K. Polycrystalline tungsten tips were prepared in situ by self-sputtering and annealing. Adsorbates were introduced into the chamber via a capillary array doser attached to a variable leak valve. The O₂ molecules were adsorbed on the sample at 45 K to ensure molecular chemisorption. The O₂ coverage was kept below 0.01 monolayer (ML) to permit investigation of individual well-isolated molecules. Coadsorption of ethylene and acetylene molecules onto the Ag(110) surface at coverages of less than 0.01 ML was performed at either 13 or 45 K. Atomically resolved imaging was achieved by transferring an ethylene molecule to the tip at 13 K.³⁰

Figure 1a shows a constant-current STM image taken with a bare metallic tip of one physisorbed ethylene and two chemisorbed oxygen molecules. The ethylene molecule appears as an oval-shaped protrusion elongated along the [001] direction on Ag(110) under typical imaging conditions, while the oxygen molecules appear as an oval-shaped depression elongated along the [110] direction. Atomically resolved imaging the same area using an ethylene-terminated tip (Figure 1b) established that ethylene binds at the atop site, in agreement with previous theoretical calculations.³¹ Previous studies have examined the structures of ethylene adsorbed on Ag(110) surfaces.³²⁻³⁷ Using high-resolution electron energy spectroscopy (HREELS), Backx et al.³²⁻³⁴ revealed that (i) ethylene adsorbs onto Ag(110)
Theoretical calculations predict that adsorption of ethylene is along the [110] direction, with the oxygen atoms. The C–C axis parallel to the [110] direction of the substrate [O2(001)] and the other with the molecular axis aligned along the [110] direction [O2(110)] (Figure 1c). We note that the O2(110) molecule is slightly more depressed than the O2(001) molecule in the topographical image. The O2(001) irreversibly rotates to the O2(110) by applying a bias voltage pulse.

Two predominant types of chemisorbed O2 have been identified, one with the molecular axis aligned along the [001] direction of the substrate [O2(001)] and the other with the molecular axis aligned along the [110] direction [O2(110)] (Figure 1c). We note that the O2(110) molecule is slightly more depressed than the O2(001) molecule in the topographical image. The O2(001) irreversibly rotates to the O2(110) by applying a bias voltage pulse.

The ethylene molecule is weakly adsorbed on Ag(110), which enables a precise manipulation both vertically (between the STM tip apex and the surface) and laterally (on the surface) by maintaining the appropriate sample bias voltage and tunneling current at a substrate temperature of 13 K. For vertical transfer from the surface to the tip, the bare metallic tip was positioned above an ethylene molecule with the junction set by a tunneling current at a sample bias voltage of 70 mV. While the feedback loop was kept on, the bias was flipped to +140 mV. The tunneling current was then ramped from 0.1 to 10 nA to induce the transfer of ethylene to the tip. The resulting ethylene-terminated tip can then be used for atomically resolved imaging (Figure 1b). The enhanced spatial resolution achieved using this tip may be attributed to either overlap between the spatially localized molecular orbital of the ethylene at the tip apex with the electronic states at the surface or the higher resistivity of the ethylene on the tip compared to the bare tip.

The ethylene was moved laterally at 13 K by applying a positive sample voltage pulse of ~250 mV when feedback was set by a tunneling gap over the molecule at a sample bias voltage of 70 mV and a tunneling current of 1 nA. The...
At 45 K, the same complexes can be produced by thermal diffusion of ethylenes: 84.6% of the complexes are formed in a metastable configuration with a low energy barrier for conversion to the C2H4-O2(110) complex.

The orientation of O2 molecules of the complexes was determined by using STM inelastic electron tunneling spectroscopy (STM-IETS). A study of the C2H4-O2(001) and C2H4-O2(110) complexes using STM-IETS revealed that the O2(001) of the C2H4-O2(001) complexes exhibits two vibrational modes, whereas the C2H4-O2(110) complexes exhibit no such modes.40

In our previous STM-IETS study of O2, it was shown that isolated O2(001) but not O2(110) gives rise to vibrational modes.39

Complexes involving two ethylenes and one oxygen can also be created by moving an additional ethylene into the vicinity of the C2H4-O2(110) complex to form the two types of (C2H4)2-O2(110) complexes shown in Figures 2 and 3. In the complex shown in Figure 2, both ethylene molecules are bonded to nnt sites ((C2H4)2nnnt-O2(110)), whereas the complex shown in Figure 3 consists of one nnt and one nnnt ethylene ((C2H4)nnnt-O2(110)-C2H4nnnt). Four types of geometrical configuration were observed for the former and twelve types for the latter. In these configurations, the two ethylenes do not reside on neighboring Ag atoms due to the repulsive interaction between the ethylene molecules. The (C2H4)nnnt-O2(110) complex could be changed to the C2H4nnnt-O2(110)-C2H4nnnt complex by applying sample voltage pulses, but the reverse was not observed.
Attachment of three ethylene molecules to the O$_2$(110) led to the formation of either (C$_2$H$_4$)$_{3-}$O$_2$(110) or (C$_2$H$_4$)$_{2-}$O$_2$(110) complexes. Further, attachment of four ethylene molecules to the O$_2$(110) gave rise to the complexes shown in Figure 6, where both configurations were observed for the former and two for the latter. Only one configuration was observed for the former complex and two configurations for the latter complex.

In the gas phase, the interaction between O$_2$ and ethylene is so weak that the molecules do not form complexes. The present STM results and previous ab initio density functional theory calculations indicate that the complexes formed between O$_2$ and ethylene on a silver substrate are stabilized by hydrogen bonding between a C-H group of the ethylene and O$_2$. The calculated bond distances are 2.79 and 2.76 Å for (C$_2$H$_4$)$_{3-}$O$_2$(110) and (C$_2$H$_4$)$_{2-}$O$_2$(110), respectively. These hydrogen bonds result from adsorption-induced electron transfer to the O$_2$, which enhances the electrostatic interaction between the oxygen molecule and the hydrogen of ethylene.

Figure 7 shows the complexes formed between acetylene and O$_2$(110) at 13 K; acetylene is highly mobile even at 13 K and spontaneously diffuses to the O$_2$(110) to form complexes. Either one (parts a and b of Figure 7) or two (Figure 7c) acetylene molecules can bind to the O$_2$(110). The adsorption position of the acetylene of the complex is determined to the nearest-neighbor fourfold hollow site by high-resolution imaging using an ethylene-terminated tip. The acetylene in the monoacetylene complex can be translocated around the O$_2$(110) by applying sample voltage pulses. In these images, the acetylenes in the complexes appear blurry and with two prominences, possibly due to fluctuation of the hydrogen atoms.

The hydrogen bond strength depends on the hybridization of the donor carbon atom and the acidity of the donor C-H group according to the calculations. Generally, the sp hybridization of alkynes allows the C-H group to form a more attractive interaction with a proton acceptor, rather than alkenes. On a solid surface, however, the adsorption geometry should be also considered. When acetylene is adsorbed on Ag(110), its hydrogen atoms are not directed parallel to the surface, which may disturb the formation of hydrogen bonds.
In summary, we first observed various configurations of the (C₂H₄)x−O₂ (x = 1 − 4) and (C₂H₂)x−O₂ (x = 1 and 2) complexes adsorbed on Ag(110). In these complexes, ethylene is bound to O₂ through C−H···O hydrogen bonds. An initial pathway for the reactants can be an important factor for the epoxidation and combustion reactions. Our observations, which may be involved in the initial states of either epoxidation or complete oxidation reaction pathways, provide an excellent starting point for the theoretical understanding aimed at elucidating the selectivity of oxidation reactions at silver surfaces.

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References and Notes

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