

LETTERS

Chemical Recognition at an Atomically Flat Surface of Metal Oxide

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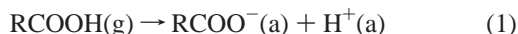
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An adsorbate monolayer composed of acetate (CH_3COO^-) and formate (HCOO^-) was prepared on an atomically flat surface of titanium oxide as a two-dimensional analogue of substituted solid solution. When the mixed-monolayer was exposed to acetic acid (CH_3COOH) vapor, an impinging acid molecule recognized a preadsorbed acetate among a lot of formates and replaced one of its formate neighbors. Straight chains of acetate were assembled in the monolayer as a result. A bimolecular intermediate state of the gas-adsorbate exchange was proposed to kinetically control which formate to be replaced.

Introduction

Recognition of one chemical species among resembling entities is a fundamental function of biological systems. Efforts have been made to artificially reproduce well-prepared mechanisms in nature. A received concept is thermodynamic recognition driven by the steric match of host and guest substances. As an example, synthesized zeolite of various pore sizes is utilized in petroleum industry to yield size-selective hydrocarbons. Advanced shape-selective recognition was recently achieved in polymers imprinted with a template macromolecule.¹ The present letter reports another scheme of chemical recognition that works with simplest organic molecules adsorbed on an atomically flat surface of metal oxide.

The (110) surface of rutile TiO_2 , the substrate, is a prototype of atomically flat surface of metal oxide.²⁻⁴ When a $\text{TiO}_2(110)$ surface is prepared in an ultrahigh vacuum and exposed to carboxylic acid (RCOOH) vapor at room temperature, carboxylate anion and proton are produced on the surface in the dissociation reaction



where (g) and (a) represent gas phase and adsorbed phase.⁵ Each

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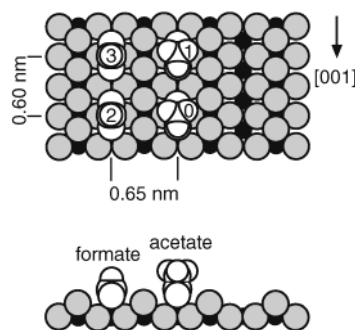
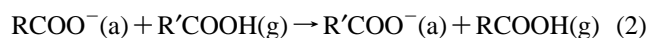


Figure 1. Formate and acetate chemisorbed on the $\text{TiO}_2(110)$ surface. White balls of van der Waals radii represent the molecular adsorbates. A right-hand side row of Ti atoms is unoccupied for illustration. The proton released in reaction 1 is not shown. Three carboxylates are numbered in the order of the distance from one numbered as 0.

carboxylate is chemically adsorbed on two Ti atoms in a bridge structure with its $\text{R}-\text{C}$ bond perpendicular to the surface⁶⁻⁹ as illustrated in Figure 1. When the bridge-adsorbed carboxylates fully occupy the Ti atoms, a long-range ordered monolayer is spontaneously formed. Subsequent exposure to another carboxylic acid ($\text{R}'\text{COOH}$) vapor causes the exchange of preadsorbed and incoming carboxylates¹⁰



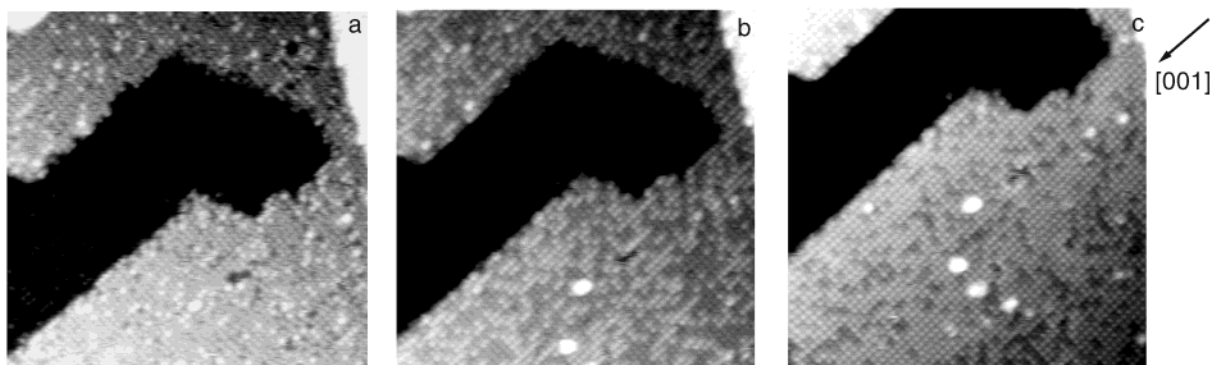


Figure 2. STM topography of a formate monolayer on $\text{TiO}_2(110)$ being exchanged in acetic acid vapor. A formate-covered surface maintained at room temperature was exposed to acetic acid vapor (1×10^{-7} Pa) at $t = 0$. Frames a, b, and c were observed at $t = 21$, 287, and 565 s in the vapor atmosphere, respectively. Image size: $35 \times 35 \text{ nm}^2$, sample bias voltage: +1.0 V, tunnel current: 0.4 nA.

A particular case of acetate ($\text{R}'=\text{CH}_3$) replacing formate ($\text{R}=\text{H}$) was examined in the present study by scanning tunneling microscopy (STM).

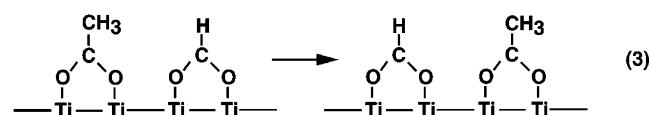
Experimental Section

Experiments were performed using an ultrahigh-vacuum-compatible microscope (JEOL, JSPM-4500S) with a liquid nitrogen bottle for sample cooling. A platinum resistance thermometer (Sensycon, GR2105) was clamped with a $\text{TiO}_2(110)$ wafer to achieve precise control of the temperature. The formate-covered surface was prepared by exposing a sputter-annealed (1×1) surface to formic acid vapor at room temperature. Constant current topography was sequentially observed at an acquisition rate of 6 s per frame with an electrochemically etched tungsten tip in the presence or absence of acetic acid vapor.

Results and Discussion

The exchange reaction was thermally activated at temperatures of 190 K or above. Figure 2 presents sequential STM images observed on a formate-covered surface exposed to acetic acid vapor at room temperature. Two molecules of different brightness were resolved as bumps. The bright species, the number of which increased with the exposure time, was assigned to acetate. The exchange reaction occurred over the surface without preference at step edges of the substrate, in contrast to NO dissociation catalyzed at steps on $\text{Ru}(0001)$.¹¹ The long-range order of the adsorbates remained intact at any acetate/formate ratio. Our adsorbates with nearly equivalent terminal groups (H or CH_3) yielded a two-dimensional crystal as if they were identical entities. This mixed-layer of adsorbate thus provides a two-dimensional analogue of substituted solid solution known in the three-dimensional world.

Examine the lateral distribution of acetates embedded in the preadsorbed monolayer of formate. Short rows of acetate parallel to the $[001]$ direction were identified on the mixed-monolayer being exchanged (Figure 2b). The acetate distribution at room temperature was, however, affected (probably randomized) by the lateral exchange of adsorbed carboxylates

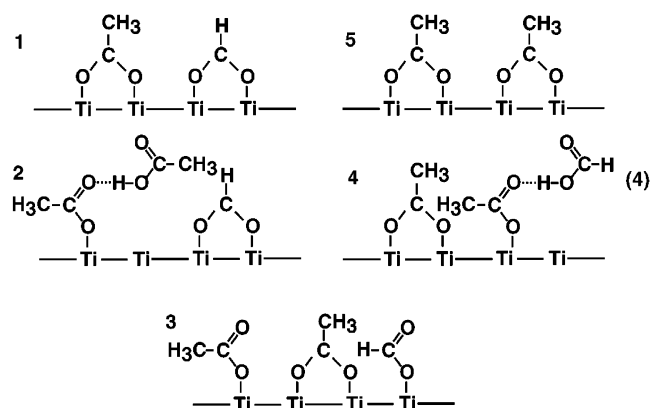


This reaction was activated at 220 K and competed with reaction

2 on the surface of Figure 2. See the microscope movie as Supporting Information.

To minimize the contribution of reaction 3, another formate-covered TiO_2 surface was cooled at 196 K and exposed to acetic acid vapor. Long, straight chains of acetate appeared parallel to the $[001]$ direction on the surface. The longest chain in Figure 3, the ends of which are marked by arrowheads, contained 17 acetates. Each CH_3COOH molecule incoming from the gas phase must have recognized a preadsorbed acetate and replaced one of its formate neighbors. The lateral distribution of acetate represented where the gas-adsorbate exchange had taken place, because reaction 3 was prohibited at this low temperature. The frequency of reaction 3 at 196 K was determined to be less than $2 \times 10^{-4} \text{ min}^{-1}$ in a separate observation, where 450 carboxylates remained stationary for 14 min. The surface of Figure 3 was, on the other hand, prepared and then imaged within 13 min. The surface diffusion could not be important in assembling the chains.

We have already proposed a trap-and-insertion mechanism of the gas-adsorbate exchange reaction 2; A $\text{R}'\text{COOH}$ impinging from the gas phase is trapped on an adsorbed RCOO^- with a hydrogen bond and inserted into the monolayer to produce an adsorbed $\text{R}'\text{COO}^-$. One of the RCOO^- neighbors is then eliminated in the reverse reaction of the insertion to complete the exchange. The individual steps were resolved in our previous study.¹² The self-directed growth of the acetate chain observed in Figures 2 and 3 is interpreted with the following scheme based on the trap-and-insertion mechanism.



Small number of acetates are preadsorbed in the formate monolayer when a CH_3COOH encounters the surface (state 1). The incoming molecule is preferably trapped on a preadsorbed

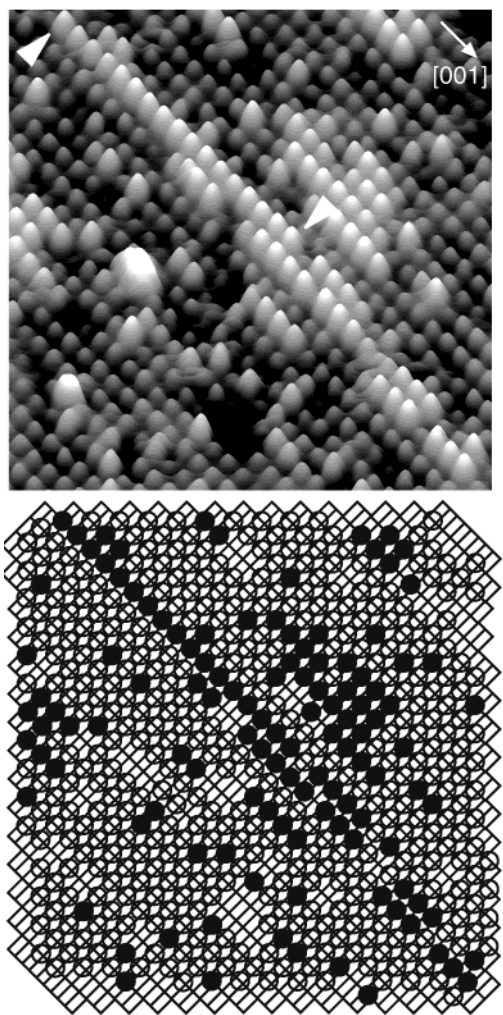


Figure 3. Straight chains of acetate embedded in a formate monolayer on TiO₂(110). A bird's eye view of STM topography of the formate monolayer exposed to acetic acid vapor (2×10^{-7} Pa) at 196 K. The identity of the carboxylates is shown in the lower panel with filled (acetate) and open (formate) marks superimposed on the Ti-atom mesh of the substrate.

acetate rather than on a formate via a hydrogen bond (state 2). The trapped CH₃COOH is dissociated and inserted in the monolayer to yield a bridge-adsorbed acetate (state 3). Two preadsorbed carboxylates reconstruct in a monodentate form, where one carboxylate occupies one Ti atom, to make room for the inserted acetate. The monodentate formate is pushed out of the chemisorbed layer as a hydrogen-bonded HCOOH (state 4) and finally released into the gas phase (state 5). By repeating the five steps, a straight chain of acetate is assembled in the monolayer of formate. This proposed scheme was evidenced by an STM image of acetate monolayer exposed to acetic acid vapor at 174 K (Figure 4). Two molecules of different topography were resolved with a bridge-adsorbed acetate between and assigned to the all-acetate analogue of state 3.

It is essential in this scheme that a CH₃COOH–acetate complex is more stable and thus more frequently formed at state 2 than a CH₃COOH–formate complex. How is the CH₃COOH–acetate complex stabilized? We cannot expect steric preferences in the carboxylate monolayer synthesized on the atomically flat surface. Instead, the hydrogen bond can be strengthened in the CH₃COOH–acetate complex due to the electron donation from the methyl substituent. An MP2 calculation was done with 6-311+G** basis set on the GAUSSIAN98 program¹³ to

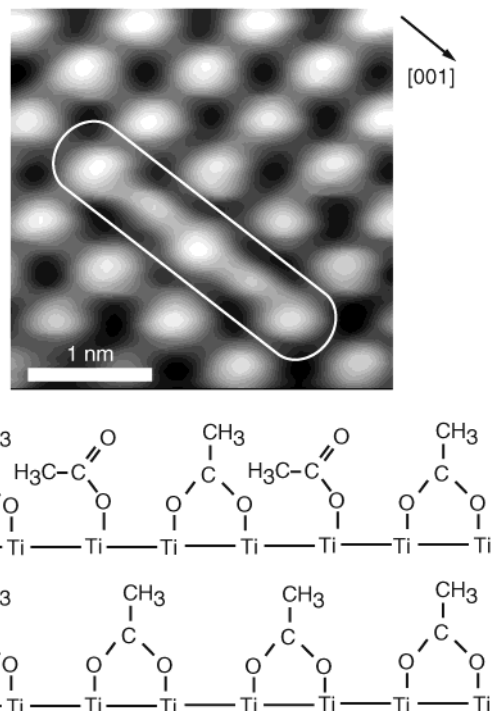
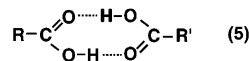


Figure 4. An acetate monolayer inserted by an excess acetate. A monolayer of bridge-adsorbed acetate was exposed to acetic acid vapor at 150 K and then heated at 174 K in a vacuum to remove physisorbed molecules. Two monodentate-adsorbed and three bridge-adsorbed acetates are marked with white line in the STM image and illustrated in the lower panel. Four acetates bridge-adsorbed on eight Ti atoms are drawn for comparison.

examine this idea. Two carboxylic acid molecules are known to make a dimer via two hydrogen bonds



The calculated energy gain by dimerization of CH₃COOH–HOOCCH₃, CH₃COOH–HOOCH, and HCOOH–HOOCH was 678, 660, and 637 meV, respectively. The predicted energy gain was around 0.6 eV and consistent with the reported residence time of state 2 (order of 10 s at 193 K)¹² by assuming a standard preexponential factor of 10^{13} s^{−1}. The energy gain was sensitive to the chemical identity of the terminal groups. The CH₃COOH–HOOCCH₃ dimer was stabilized by 18 meV in comparison with the CH₃COOH–HOOCH dimer. We expect a parallel stability on the bimolecular complex of state 2 containing one hydrogen bond. When the CH₃COOH–acetate complex on the surface is more stable by 0.01 eV than the CH₃COOH–formate complex, its population is thermodynamically enhanced by a factor of 2 at 196 K.

The predicted enhancement agreed with the experimental result. The number of acetate accompanied by another acetate at its nearest neighbor position was 64 in Figure 3, while the imaged area contained 122 acetates and 377 formates. If each acetate randomly exchanged a formate, the number of the accompanied acetates would be $30 = 122^2 / (122 + 377)$. The frequency of the nearest-neighbor exchange was thus enhanced by 2.1 times.

The qualitative agreement of observed and predicted enhancements supported our scheme of the nonsteric recognition of an acetate over many formates. The bimolecular intermediate state determined which carboxylate was to be reacted. Appropriate selection of the terminal groups may lead to more

advanced, self-directed assembly of substituted carboxylates on metal oxide, an important class of materials with optical transmittance, high dielectric constants, and biocompatibility. Early examples of self-directed molecule assembly were limited on surfaces of Si,¹⁴ graphite,¹⁵ and metals.^{16–18}

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Supporting Information Available: An STM movie of the surface of Figure 2 is available as a QuickTime file. Constant current topography was sequentially determined with an acquisition time of 12 s frame⁻¹ in the presence of the acetic acid atmosphere. Image size: 35 × 35 nm², sample bias voltage: +1.0 V, tunnel current: 0.4 nA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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