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Deciphering Adsorbate–Adsorbate Interactions from Scanning Tunneling Microscopy Images: Integrated Topological, Statistical, and First- Principles Analysis of Methoxy Adsorbates on Pt/TiO₂(110)

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ABSTRACT: Adsorbate–adsorbate interactions and their distributions are fundamentally important to attaining an atomic-level understanding of heterogeneous catalysis. Scanning tunneling microscopy (STM) is one of the most powerful evaluation techniques because it can image individual atoms or molecules and give their distribution on a solid surface. Once the adsorbate locations are determined, a two-dimensional (2D) radial distribution function, which provides the azimuth and distance of one adsorbate relative to another, can be obtained to evaluate the lateral interactions between the two adsorbates. However, when adsorbates are distributed on different terraces and other adsorbates are present on the surface, automatically determining the adsorbate locations is challenging. Here, we applied topological data analysis using persistent homology to STM images of methoxy adsorbates on a Pt/TiO₂(110) surface, and the locations of each methoxy adsorbate were selectively identified. We then calculated the 2D radial distribution function and found that occupation of the adjacent methoxy adsorbate at the nearest and 2nd nearest adsorption sites was significantly suppressed, indicating a repulsive interaction between them. Density functional theory calculations attributed this to steric hindrance between neighboring methyl groups and electrostatic repulsion between the methoxy adsorbates, resulting in destabilization in the adsorption energy. The distribution of methoxy adsorbates was well reproduced by Monte Carlo simulations using a one-dimensional random walk model, assuming that it followed the Boltzmann distribution depending on the adsorption energy and temperature. Our integrated topological, statistical, and first-principles approach is effective for visualizing and understanding adsorbate–adsorbate interactions using STM images and can be applied to various adsorbate systems.

1 INTRODUCTION

Adsorbate–adsorbate interactions on solid surfaces play a crucial role in determining molecular arrangement, overlayer stability, and surface reactivity.^[1-3] Together with the adsorbate–substrate interactions, they considerably affect the formation of surface phases, for example, the ordered structures of adsorbed molecules and their mobility. The adsorbate–adsorbate interactions can be classified into short-range and long-range types, depending on their decay with intermolecular distance (d).^[4,5] At short range, the van der Waals interaction provides a universal attraction arising from instantaneous charge fluctuations, typically decaying as d^{-6} . At very close proximity, overlapping electron clouds generate strong exchange repulsion (steric hindrance). In the long-range regime, electrostatic effects, often described as Coulomb interaction, become dominant. A key manifestation is the dipole–dipole interaction between adsorbates, where the relative orientation of dipoles determines whether the interaction is attraction or repulsion. Favorable alignment can stabilize dense molecular layers, while unfavorable alignment increases intermolecular spacing. The competition between van der Waals attraction at short separations and electrostatic dipole–dipole or Coulomb interaction at longer distances governs the equilibrium intermolecular distance and ordering of adsorbates. Understanding this balance is essential for controlling catalytic reactions, molecular self-assembly, and thin-film growth.

The chemistry of methanol on rutile $\text{TiO}_2(110)$ has been extensively studied^{6–14} because the interaction of this small alcohol with the TiO_2 surface is important for several applications in heterogeneous catalysis and photochemistry. Methoxy intermediates have been reported to form on fivefold-coordinated Ti (Ti_{5c}) sites at room temperature by exposing a $\text{TiO}_2(110)$ surface to O_2 gas and then to methanol vapor, followed by heating at 350 K.¹⁴ These methoxy intermediates thermally decompose into formaldehyde and methanol by the disproportionation reaction between two adjacent methoxy intermediates. On the other hand, the addition of Pt

nanoparticles onto a $\text{TiO}_2(110)$ surface also produces methoxy intermediates on the Ti_{5c} sites at room temperature by exposure of the $\text{Pt/TiO}_2(110)$ surface to methanol vapor.¹⁵ They are formed by the dissociation of methanol molecules on the Pt sites and then spillover to the Ti_{5c} sites. In the presence of Pt nanoparticles, most of the methoxy intermediates thermally decompose into CO (dehydrogenation) and CH_4 (C–O bond scission) on the Pt sites at >350 K by their diffusion and reverse spillover.¹⁶ In the low-temperature range (350~500 K), formaldehyde and methanol are also formed as minor products by partial dehydrogenation of the methoxy intermediates and by recombination of the methoxy species ($\text{CH}_3\text{O-Pt}$) and hydrogen (H-Pt), respectively, while in the high-temperature range (>500 K), they are produced by the disproportionation reaction. The activity and product selectivity for the thermal decomposition of the methoxy intermediates on the $\text{Pt/TiO}_2(110)$ surface significantly depend on the density of the Pt nanoparticles, which indicates that methoxy–methoxy interactions and the mobility of the methoxy intermediates control the decomposition properties.

Several experimental techniques can be used to characterize the adsorbate–adsorbate interactions and the distribution of the adsorbates. Low-energy electron diffraction (LEED) is the technique most frequently used for observing the two-dimensional (2D) ordering of adsorbates and for determining their structures by analyzing the intensity–energy (I–V) curve of the diffraction spots. However, the LEED method is no longer effective on surfaces without a long-range order. Scanning tunneling microscopy (STM) is one of the most powerful techniques for imaging individual atoms or molecules on a solid surface and obtaining a 2D distribution of them.

In STM image analysis, image analysis software such as WSxM¹⁷ and Gwyddion¹⁸ are often used to determine the location, size, shape, and number of bright spots, such as adsorbates and nanoparticles distributed on a surface. The distribution of adsorbates can be converted into a

radial distribution function that reflects the effective lateral interaction between them. However, the topological features of the alignment of adsorbates cannot be quantified using conventional approaches, although they provide crucial information for understanding the surface reaction processes. Furthermore, determining the adsorbate locations to obtain the radial distribution function is challenging. For instance, automatically determining the adsorbate locations using threshold segmentation based on absolute image intensities—even after applying conventional image analysis software to adjust the image contrast and enhance the position—is often difficult, particularly when they are distributed on different terraces and other adsorbates or nanoparticles are present on the surface. Another difficulty is identifying the position (pixel) of the adsorbate from the bright spots (pixels) in the STM image, particularly when its shape deviates from a precise circle.

Persistent homology (PH) is a method used in topological data analysis (TDA) to quantify the shape of data^{19,20} and has recently been applied in the analysis of microscope images to obtain quantitative information on specific regions or features in the images.^{21,22} For STM images, surface-supported covalent networks have been investigated using PH²¹, but only the perfectness of ordering was considered. In the present study, we used TDA with PH to analyze the STM images of methoxy adsorbates on a Pt/TiO₂(110) surface and successfully determined locations of each methoxy adsorbate in the images. This study is the first to apply PH to characterize the spatial behavior or topological features of adsorbed molecular species using STM height information. A 2D autocorrelation function (radial distribution function) was then calculated for the locations of the methoxy adsorbates to elucidate the lateral interactions between them. We observed repulsive interaction between neighboring methoxy adsorbates, particularly when they were located on the nearest and 2nd nearest Ti_{5c} sites. Density functional theory (DFT) calculations and Monte Carlo simulations were performed to reveal the origin of the repulsive interaction and reproduce the distribution of the methoxy adsorbates. We propose

a methodology to evaluate adsorbate–adsorbate interactions from STM images, which consists of selective detection of adsorbate locations by PH analysis, conversion of the adsorbate distribution into the radial distribution function, and a theoretical approach to understanding the origin of the adsorbate–adsorbate interactions.

2. METHODS

2.1. Sample preparation and STM measurements. The as-received rutile-TiO₂(110) wafer (7×3×0.5 mm; Shinkosha Co., Japan) was immersed in a 10% HF solution and then calcined in air at 1100 K for 12 h.^{23,24} After being loaded into the preparation chamber of the ultra-high vacuum (UHV) STM apparatus (JEOL JSPM4500S), the surface was cleaned by cycles of Ar⁺ sputtering (2 keV) and annealing (1000 K). Pt was deposited at room temperature through the electron bombardment of a Pt rod (99.98%, Nilaco Co., Japan) with the application of a high voltage (typically 850 V) between the filament and the Pt rod. The Pt coverage was estimated to be 0.04 ML based on X-ray photoelectron spectroscopy measurements, where 1 ML was defined as the density of the (1×1) units of the TiO₂(110) surface (i.e., $5.2 \times 10^{18} \text{ m}^{-2}$). The Pt/TiO₂(110) surface was then annealed at 473 K for 10 min to obtain a uniform size distribution of Pt nanoparticles. Methanol (Superpure reagent grade, Fujifilm Wako Chemicals, Japan) was purified by several freeze–pump–thaw cycles using liquid nitrogen prior to its introduction onto the Pt/TiO₂(110) surface and was dosed at room temperature through a variable leak valve by backfilling. Constant current-mode STM measurements were conducted using an electrochemically etched W tip at room temperature. The sample bias voltage (V_s) and the tunneling current (I_t) were +1.5~2.0 V and 0.1~0.2 nA, respectively.

2.2. PH analysis of STM images. PH quantitatively describes topological features such as islands or holes caused by the birth and death of shapes through filtration. The distribution of birth–death pairs indices is shown in the persistence diagram (PD). Each birth–death pair in

PD, which corresponds to a specific shape, can be projected back into the original image with the inverse analysis. Consequently, the topological features can be easily understood in real space (i.e., “white-box” approach). The details are explained by Obayashi *et al.*²⁰ The zero-dimensional (0D) PH, which can quantitatively evaluate the islands and connected components, was applied to detect the location of the methoxy adsorbates in the grayscale STM images (TIFF files) of the Pt/TiO₂(110) surfaces after methanol exposure. The grayscale ranged from 0 to 255, which corresponds to the height information. The superlevel set method was applied to the STM images in this study.²⁵ The brightness threshold for the detection of bright spots was moved from 255 to 0 by monitoring the birth and death of the methoxy species and Pt nanoparticles in the superlevel set PH analysis (Figure 2(a) and Figure S1). In this study, birth was defined as the appearance of isolated islands, corresponding to the brightest point (pixel) of the adsorbates, Pt nanoparticles, other minor species such as Ti suboxide (TiO_x, $x < 2$), or the flat terraces without any of these. Death was defined as the connection of islands corresponding to the nearest adsorbate, Pt nanoparticles, or terrace. Consequently, the PD (Figure S1(b)) was obtained, where the x- and y-axes correspond to the birth and death brightness (or height) of the methoxy adsorbates or Pt nanoparticles, respectively. The “lifetime”, defined as the difference between birth and death, was used to identify the species. To identify the locations of the methoxy adsorbates, their birth positions were plotted in the STM images using inverse analysis. The 0D PD was calculated using Python 3.9 codes with the HomCloud library.²⁶ The Gaussian blur filtering with a 5×5 pixel kernel and auto-optimized σ (1.1 in case of 5×5 kernel size) by the OpenCV library were applied to reduce image noises prior to the calculation. The calculation required ~40 s for one STM image, including pretreatment, placing the markers at adsorbate positions in the original STM image and exporting the positions as text files using a general Laptop with Jupyter Notebook environment.

2.3. DFT calculations. DFT calculations were performed using VASP 5.4^{27–30} with the projector augmented wave and plane-wave basis set methods.³¹ The kinetic energy cutoff for plane-wave expansion was set to 400 eV, and the exchange-correlation interaction between electrons was described by the Perdew–Burke–Ernzerhof functional.^{32,33} TiO₂(110) surfaces were modeled as a five TiO₂ trilayer slab with an (8×2) unit cell. The vacuum layer was 20 Å. The bottom two layers were fixed throughout the calculations, while the upper three trilayers and the adsorbates were relaxed using a quasi-Newton algorithm until the energy difference was less than 10^{−6} eV. The k-point mesh was set as 1×2×1. A van der Waals correction was applied using the Grimme DFT-D3 method with a zero-damping function.³⁴ The adsorption energy (E_{ad}) of methanol on TiO₂(110) was calculated as

$$E_{\text{ad}} = E_{\text{TiO}_2+\text{methanol}} - E_{\text{TiO}_2} - E_{\text{methanol}} \quad (1)$$

where E_{TiO_2} , E_{methanol} , and $E_{\text{TiO}_2+\text{methanol}}$ are the total electron energies of TiO₂(110), gaseous methanol, and TiO₂(110) after methanol adsorption, respectively. For pairs of methanol molecules on the TiO₂(110) surface, E_{ad} was calculated as follows:

$$E_{\text{ad}} = \frac{1}{2} (E_{\text{TiO}_2+2\times\text{methanol}} - E_{\text{TiO}_2} - 2E_{\text{methanol}}) \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Methoxy adsorbates on Pt/TiO₂(110) surface. Figure 1(a), (b) shows STM images of the Pt/TiO₂(110) surface after methanol adsorption. In addition to the Pt nanoparticles, whose average diameter and height were 2.2 ± 0.4 nm and 0.5 ± 0.2 nm, respectively, the bright spots attributed to methoxy adsorbates were uniformly distributed on the Ti_{5c} rows of the TiO₂(110) surface. The coverage of the methoxy adsorbates was 0.14 ML, and their height and lateral size were ~ 0.18 nm and ~ 0.50 nm, respectively. They were produced by dissociation of methanol molecules on the Pt sites and then spillover to the TiO₂ surface.¹⁵ Notably, methoxy coverage saturates at 0.15 ± 0.01 ML and does not increase further when methanol adsorption is

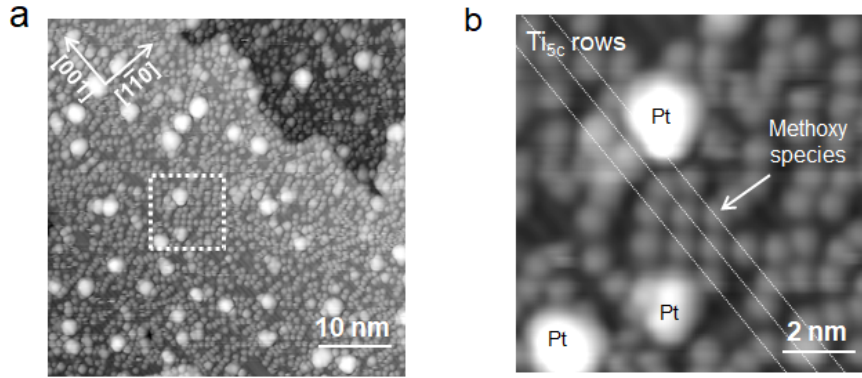


Figure 1. STM images of the Pt/TiO₂(110) surface after 5 L exposure to methanol vapor at room temperature. (a) 50 × 50 nm². (b) Magnified image (10 × 10 nm²) of the white-dotted square region in (a).

conducted at the methanol vapor pressure ranging from 10⁻⁶ to 10⁻⁸ Pa, even when the methanol dose or Pt nanoparticle density increases. These results may indicate that the saturation coverage is determined by the balance between the chemical potential of the adsorbing species and the repulsive interactions between the adsorbates. The sequential STM imaging of the methoxy adsorbates in the previous study showed that they were mobile at room temperature and diffused on the Ti_{5c} sites along the [001] or [1 $\bar{1}$ 0] direction.¹⁶ The rate constants for diffusion (diffusion coefficient, D [m²·s⁻¹]) along the [001] and [1 $\bar{1}$ 0] directions were estimated, where D can be expressed as $D = D_0 \exp(-E/k_B T)$, and D_0 , E , k_B , and T are the pre-exponential factor, activation energy, Boltzmann constant, and temperature, respectively. The D_0 values for diffusion along the [001] and [1 $\bar{1}$ 0] directions were determined to be 2×10^{-7} m²·s⁻¹ and 9×10^{-10} m²·s⁻¹, respectively, and the E values were calculated to be 0.86 eV and 0.76 eV, respectively. The D_0 value for [001]-diffusion was more than two orders of magnitude higher than that for [1 $\bar{1}$ 0]-diffusion, indicating that the former was dominant.

3.2. Determination of methoxy adsorbate positions and analysis of their topological features. As mentioned, it is difficult to selectively detect target spots in the presence of other spots originating from different adsorbates or particles and when the target spots are distributed

on different terrace surfaces, such as for methoxy adsorbates on the Pt/TiO₂(110) surface (Figure 1(a)). To solve these difficulties, TDA was applied to the STM images to selectively determine the locations of the methoxy adsorbates. Using the superlevel-set method²⁵ (Figure 2(a) and Figure S1), PH was applied to analyze the STM image. As shown in Figure 2(a), the brightness threshold for detecting the islands (bright spots) moved from 255 to 0 while monitoring the birth and death of the islands. The islands corresponding to Pt nanoparticles appear at high threshold brightness values, and the islands corresponding to methoxy adsorbates on the same terrace appear at lower values because the Pt nanoparticles are taller than the methoxy adsorbates in the STM image. These islands are dead on the terrace of the substrate or are connected to neighboring adsorbates. The birth–death pairs of islands are shown in the 0D PD (Figure 2(b)). Each data point corresponds to bright spots in the image, which can be assigned to methoxy adsorbates, Pt nanoparticles, or other minor species such as TiO_x ($x < 2$) species and impurities. Overlapping or multiplicity of points in the same (birth,

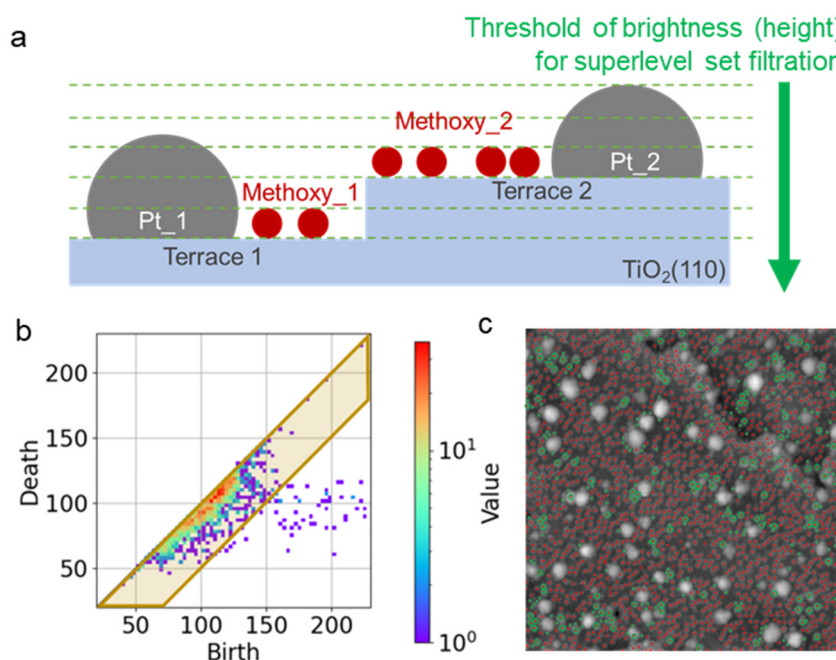


Figure 2. (a) Schematic for PH analysis with superlevel set method. (b) 0D PD for Figure 1(a). The yellow-highlighted region has a lifetime of 2–50, corresponding to the methoxy adsorbates. (c) The methoxy adsorbate positions determined by PH (red), manually (green dots), and false detection (green circles) as TiO_x species.

death) pairs in the PD are shown in color; highly populated points (red points in Figure 2(b)) show islands corresponding to methoxy adsorbates.

The adsorbates on the same terrace, schematically shown in Figure 2(a), should have the same birth and death values. However, the red points in Figure 2(b) are discretely distributed, probably owing to the tilting of the specimen substrate or terraces. In other words, the islands and their positions were successfully determined by PH, regardless of the brightness (or height). The red dots in Figure 2(c) were obtained by plotting the birth positions of the data points located within the yellow-highlighted region in Figure 2(b) (1592 spots), which is defined as the “lifetime” from 2 to 50 and corresponds to threshold setting of the height from 0.01 to 0.3 nm. Most of the methoxy adsorbates were successfully identified, even though they were distributed on different terrace surfaces and Pt nanoparticles were present. Some methoxy adsorbates (210 spots, green dots in Figure 2(c)) located close to the Pt nanoparticles were not detected and were added manually. TiO_x species (129 spots, green circles in Figure 2(c)) were also detected owing to their similar height to the methoxy adsorbates and were removed manually (see description on detection of the methoxy species by PH analysis in Supporting Information). The proposed framework is the first to apply PH to characterize adsorbed molecular species using height information from STM images. The framework can distinguish between the adsorbate and Pt nanoparticle positions and detect the adsorbate positions selectively, even when they are distributed on different terrace surfaces, which is difficult to achieve using threshold or watershed segmentation. Another advantage is its capability to determine the highest position (brightest pixel) of the adsorbate area (bright pixels) in terms of topological features.

3.3. Autocorrelation analysis of distribution of methoxy adsorbates. Since the locations of the methoxy adsorbates were successfully identified by TDA using PH, the autocorrelation of the methoxy adsorbates was calculated to examine their lateral distribution. When applied

to a microscope image, the 2D autocorrelation function $F(i, j)$ provides the azimuth and distance of one methoxy adsorbate relative to another.^{35–37} $F(i, j)$ is given by

$$F(i, j) = \sum_{i, j} (f(x, y)f(x + i, y + j))^{\frac{1}{2}} \quad (3)$$

where $f(x, y)$ denotes the image intensity at pixels (x, y) . We defined $f(x, y) = 1$ for the pixel where a methoxy adsorbate was detected, as shown in Figure 2(c), and set $f(x, y) = 0$ for the other pixels. Then, $F(0, 0)$, the sum of the self-images of each methoxy adsorbate is equal to the number of methoxy adsorbates. Here, we consider the function $F(i, j)/F(0, 0)$, which corresponds to the ratio of methoxy adsorbates that find another molecule at $F(i, j)$.

$F(i, j)/F(0, 0)$ was calculated for 13,802 methoxy species in eight $50 \times 50 \text{ nm}^2$ STM images. The obtained $F(i, j)/F(0, 0)$ map is shown in Figure 3(a), in which the central bright spot ($F(0, 0)$) was removed. Rows of bright spots were observed along the $[001]$ direction, while some spots near the central spot were missing. The distance between neighboring spots along the $[001]$ direction was 0.3 nm, and the distance between adjacent rows was 0.65 nm, which corresponded to the (1×1) lattice units of the $\text{TiO}_2(110)$ surface, that is, the location of the Ti_{5c} sites where methoxy species were present. The size and contrast of each bright spot reflect the distribution of the position and frequency of the methoxy adsorbates found at the corresponding Ti_{5c} site, respectively. Figure 3(b), (c) shows the intensity profile along the white-dotted line in Figure 3(a) and the histogram of the number ratio ($F(d)/F(0)$) of the methoxy adsorbates observed at the separation distance (d) of 0.3~2.7 nm along this direction. The $F(d)/F(0)$ value was obtained by integrating the pixel intensities within the bright spot assigned to the corresponding distance. The results indicated that the adjacent methoxy adsorbates rarely occupied the nearest and 2nd nearest neighbor Ti_{5c} sites owing to their repulsive interactions. Most of them were detected at $d \geq 0.9 \text{ nm}$, and the $F(d)/F(0)$ value seems to show a maximum at approximately $d = 0.9$ and 1.2 nm. It should be noted that the results shown in

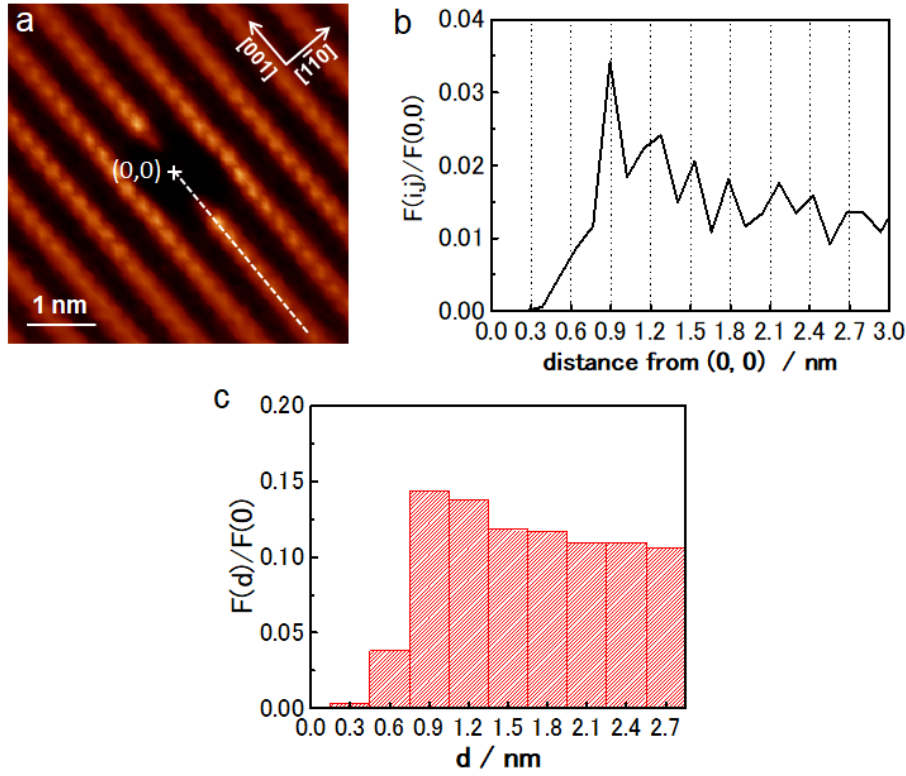


Figure 3. (a) Map of the normalized autocorrelation function ($F(i,j)/F(0,0)$) for the methoxy adsorbates on the Pt/TiO₂(110) surface (5×5 nm²). The central bright spot ($F(0,0)$) was removed. The reference point (0, 0) corresponds to a central methoxy adsorbate, and the intensity distribution reflects the positions at which additional methoxy adsorbates are identified. (b) Intensity profile along the white-dotted line in (a). (c) Histogram of $F(d)/F(0)$ value obtained for the methoxy adsorbates, which were assigned to be located at a separation distance (d) in the range of 0.3~2.7 nm along the [001] direction.

Figure 3(a)–(c) did not change significantly, even when we used the uncorrected STM images, that is, before adding the undetected methoxy adsorbates near the Pt nanoparticles and removing the TiO_x species (see Figure 2(c)). Our results clearly suggest that repulsive adsorbate-adsorbate interactions cause individual adsorbates to have an “excluded volume” that is inaccessible to other adsorbates, which helps to validate the recent development of theoretical adsorption isotherm equations assuming such repulsive interactions between the adsorbates.³⁸

No 2D ordering of the methoxy adsorbates was found, in contrast to the bidentate formates adsorbed on the TiO₂(110) surface. A short-range c(4×2) ordered structure has been obtained

by applying a similar autocorrelation analysis to the STM image of 0.11 ML formates on a $\text{TiO}_2(110)$ surface at room temperature,³⁶ where formate diffusion was not activated. The authors proposed that the electrostatic repulsion between the formate anions dominates the $c(4\times 2)$ structure. The proton bonded to the bridging oxygen (O_{br}), that is, the surface hydroxyl group produced by the dissociative adsorption of formic acid, has been proposed as a possible medium to control the 2D ordering of formates, particularly for the formate–formate interaction across the O_{br} rows by electrostatic interactions and/or hydrogen bond formation. The role of the protons may be more important for the formates with a higher coverage because the long-range (2×1) order was observed at the saturation coverage (0.5 ML).³⁹ One possible reason for the absence of 2D ordering of the methoxy adsorbates is the lack of energetic stabilization by the protons because the proton position is not fixed at a specific O_{br} atom. Our previous STM and DFT calculation results indicate that the methoxy adsorbate is mobile, hopping on the Ti_{5c} sites together with the adjacent proton at room temperature via the temporal formation of molecularly adsorbed methanol through repeated dissociation and association of the $\text{CH}_3\text{O}-\text{H}$ bond.¹⁶

3.4. Theoretical investigation of methoxy–methoxy interaction and its distribution. As shown in Figure 3, neighboring methoxy adsorbates exhibit repulsive interactions. To investigate the origin of this repulsion, DFT calculations were conducted on a $\text{TiO}_2(110)$ slab with a pair of methoxy adsorbates separated by varying distances. Figure 4 shows the optimized structures of a single methoxy species and pairs of methoxy species with varying separation distances. Previous STM and DFT calculation results showed that the dissociated H atom (proton) is located adjacent to the methoxy species in the form of a hydroxyl group.^{15,16} The proton and the methoxy anion could be energetically stabilized by the electrostatic attraction, as well as the hydrogen bond formation between the proton and the oxygen atom of the methoxy species. The calculated adsorption energies (E_{ad}) are listed in Table 1. The E_{ad} value

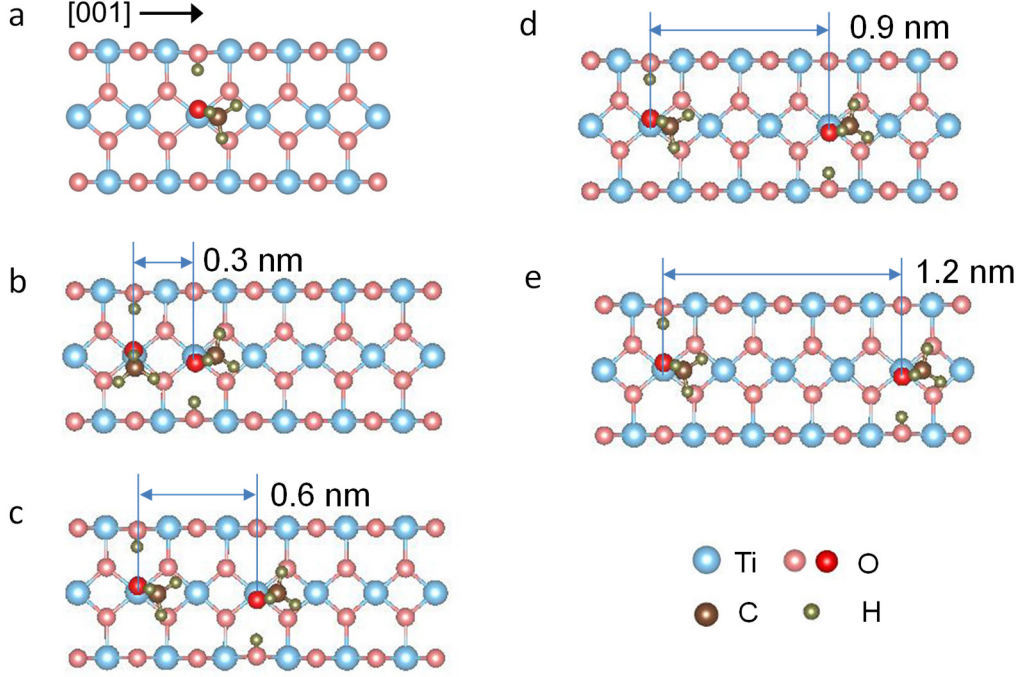


Figure 4. Optimized structures of the methoxy species adsorbed singly or as a pair on the TiO₂(110) surface. The superlattice cell was 8×2 , corresponding to the methoxy coverage of 0.125 ML. (a) Singly adsorbed methoxy species. (b)–(e) Pairs of methoxy species at varying separation distances along the [001] direction.

for a single methoxy adsorbate (Figure 4(a)) was -1.78 eV, which is more negative than the previously reported value of -1.38 eV¹⁶ due to the inclusion of van der Waals correction. The E_{ad} value became less negative as the two methoxy adsorbates approached each other, reaching a maximum at the nearest neighbor distance ($d = 0.3$ nm), indicating progressive destabilization due to repulsive interactions.

The pair-interaction energy, $E_{\text{int}}(d)$, was defined to quantitatively estimate the energetic destabilization of a methoxy adsorbate upon introducing a second one at a separation distance, d (nm):

$$E_{\text{int}}(d) = 2(E_{\text{ad,pair}}(d) - E_{\text{ad,single}}) \quad (4)$$

Here, $E_{\text{ad,single}}$ and $E_{\text{ad,pair}}(d)$ are the adsorption energies of the single methoxy species and the methoxy pair separated at d (nm), respectively. The calculated $E_{\text{int}}(d)$ values are listed in

Table 1. Adsorption energy (E_{ad}) and pair-interaction energy (E_{int}) of methoxy species on a $\text{TiO}_2(110)$ surface.

		$E_{\text{ad}} / \text{eV (per methanol)}$	$E_{\text{int}}(d) / \text{meV}$
Single methoxy species		-1.775	/
Methoxy pair	$d = 0.3 \text{ nm}$	-1.698	154
	$d = 0.6 \text{ nm}$	-1.746	59
	$d = 0.9 \text{ nm}$	-1.767	17
	$d = 1.2 \text{ nm}$	-1.768	15

Table 1; at $d = 0.3$ and 0.6 nm , the $E_{\text{int}}(d)$ values are 154 and 59 meV, respectively, much larger than those at longer separation distances. The highest $E_{\text{int}}(d)$ at $d = 0.3 \text{ nm}$ originated from the strong steric repulsion between the neighboring methyl groups, whose van der Waals diameter (0.40 nm) is larger than their separation distance (0.3 nm). As shown in Figure 4(b), one of the methyl groups (left side) was forced to move away from the most stable orientation shown in Figure 4(c)–(e). At $d \geq 0.6 \text{ nm}$, the orientations of the two methoxy species are similar, which means that a different kind of repulsive interaction is dominant. We plotted the E_{int} values as a function of d , and conducted the fitting with a power function ($E_{\text{int}} = \alpha d^\beta$, with α and β being the fitting parameters) although the number of the data points is limited, as shown in Figure S2. α and β were estimated to be 16 ± 4 and -2.5 ± 0.6 , respectively. Given that the scaling of dipole-dipole interaction follows d^{-3} ,^{5,40} while that of charge-dipole follows d^{-2} ,⁵ the repulsion between the methoxy species separated at $\geq 0.6 \text{ nm}$ may be dominated by the electric field-induced interactions such as dipole-dipole and/or charge-dipole interactions.

Monte Carlo simulations were conducted to evaluate the relationship between the methoxy–methoxy interactions and their distribution on the surface. Considering that the frequency of methoxy diffusion along the $[1\bar{1}0]$ direction is rather low, as described in the former session,

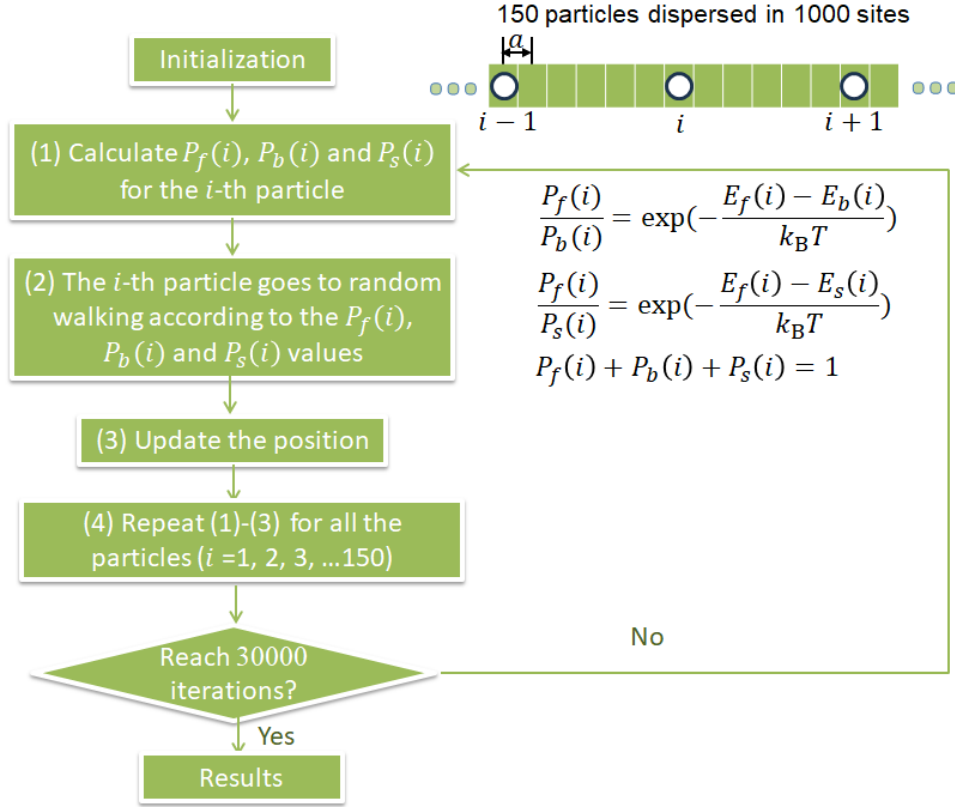


Figure 5. Flowchart of the Monte Carlo simulation based on 1D random walking, with probabilities determined by the pair-interaction energy ($E_{\text{int}}(d)$).

we focused only on [001]-diffusion and used a 1D random-walk model to reproduce the distribution of the methoxy adsorbates observed in Figure 3(c). Figure 5 shows a flowchart of the simulation. Initially, 150 particles were distributed in a row of 1000 grids (0.15 ML), where one particle was placed every six grids, with 105 vacant sites at one end. The distance between adjacent grids was $a = 0.3$ nm. Subsequently, the particles started walking randomly. In each iteration step, the movement of the i -th particle ($i = 1, 2, \dots, 150$), was considered to either stay, move forward, or move backward. The interaction energies for staying ($E_s(i)$), moving forward ($E_f(i)$), and moving backward ($E_b(i)$) for the i -th particle are defined as follows:

$$E_s(i) = E_{\text{int}}(d_{i-1,i}) + E_{\text{int}}(d_{i,i+1}) \quad (5)$$

$$E_f(i) = E_{\text{int}}(d_{i-1,i} + a) + E_{\text{int}}(d_{i,i+1} - a) \quad (6)$$

$$E_b(i) = E_{\text{int}}(d_{i-1,i} - a) + E_{\text{int}}(d_{i,i+1} + a) \quad (7)$$

where $d_{i-1,i}$ is the distance between the $(i-1)$ -th and the i -th particles, and $d_{i,i+1}$ is the distance between the i -th and the $(i+1)$ -th particles. We assumed that the $E_{\text{int}}(d)$ values are equal at $d \geq 1.2$ nm. Assuming that they follow the Boltzmann distribution, the probabilities of staying ($P_s(i)$), moving forward ($P_f(i)$), and moving backward ($P_b(i)$) for the i -th particle have the following relationship:

$$\frac{P_f(i)}{P_b(i)} = \exp\left(-\frac{E_f(i) - E_b(i)}{k_B T}\right) \quad (8)$$

$$\frac{P_f(i)}{P_s(i)} = \exp\left(-\frac{E_f(i) - E_s(i)}{k_B T}\right) \quad (9)$$

$$P_f(i) + P_b(i) + P_s(i) = 1 \quad (10)$$

By solving Equations (8)–(10), we obtain

$$P_f(i) = \frac{1}{1 + \exp\left(\frac{E_f(i) - E_b(i)}{k_B T}\right) + \exp\left(\frac{E_f(i) - E_s(i)}{k_B T}\right)} \quad (11)$$

$$P_b(i) = \frac{\exp\left(\frac{E_f(i) - E_b(i)}{k_B T}\right)}{1 + \exp\left(\frac{E_f(i) - E_b(i)}{k_B T}\right) + \exp\left(\frac{E_f(i) - E_s(i)}{k_B T}\right)} \quad (12)$$

$$P_s(i) = \frac{\exp\left(\frac{E_f(i) - E(i)}{k_B T}\right)}{1 + \exp\left(\frac{E_f(i) - E_b(i)}{k_B T}\right) + \exp\left(\frac{E_f(i) - E_s(i)}{k_B T}\right)} \quad (13)$$

The temperature (T) was set to 300 K. Then, a random number $R \in (0,1]$ was generated. When R satisfies $R \in (0, P_f(i)]$, the i -th particle moves forward, while for $R \in (P_f(i), P_f(i) + P_b(i)]$, it moves backward. In the other case of $R \in (1 - P_s(i), 1]$, the i -th particle stays. This procedure was applied to all particles and was iterated 30,000 times to obtain the equilibrium distribution of the particles. The simulation was run for 20 cycles, with each cycle including 30,000 iterations. Figure 6 shows a histogram of the average number ratio of the particle pairs separated at $d = a$ (0.3 nm) $\sim 9a$ (2.7 nm) for the 20-cycle simulation. The number ratio of the

particle pairs at a separation distance, d , was calculated by dividing the corresponding number of particle pairs by the total number of particles (150), which corresponds to the $F(d)/F(0)$ value in Figure 3(c). The occupation of adjacent particles at 0.3 nm was significantly suppressed, and only a small fraction was occupied at 0.6 nm. Most of them were found at $d \geq 0.9$ nm. The number ratio of particle pairs seemed to peak at approximately 0.9 and 1.2 nm, showing a similar distribution with the experimental results (see Figure 3(c)). Thus, the Monte Carlo simulation qualitatively reproduced the distribution of methoxy adsorbates on the Pt/TiO₂(110) surface at room temperature. The quantitative difference may be due to the difference in the local coverage of methoxy adsorbates on different Ti_{5c} rows. As described in the former session, methoxy adsorbates can diffuse along the $[1\bar{1}0]$ direction, although their frequency is low. This may cause the distribution of local methoxy coverage to depend on the Ti_{5c} rows. The presence of Pt nanoparticles and TiO₂ steps may also affect the distribution of the number of methoxy pairs because the diffusion length of the methoxy adsorbates is limited.

Although the differences in E_{ad} for methoxy pairs are relatively minor (Table 1), our Monte Carlo simulation incorporating $E_{\text{int}}(d)$ reproduced the trend of the experimental results, that

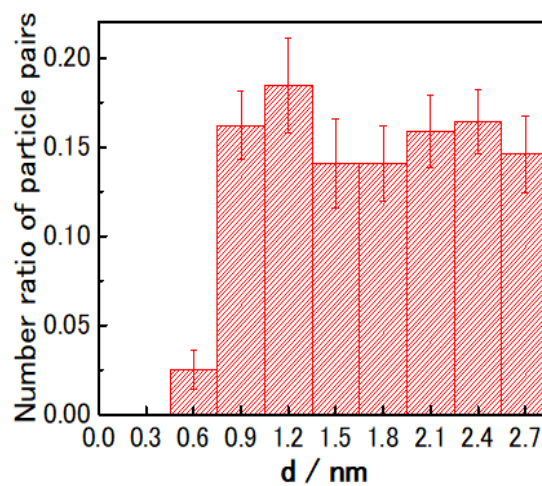


Figure 6. Histogram of the average number ratio of particle pairs observed at a separation distance (d) of 0.3~2.7 nm for the 20-cycle simulation. The standard errors of the mean (s.e.m) with 90% confidence level are included.

is, low occupation frequencies of the adjacent methoxy adsorbates at short separation distances (0.3 and 0.6 nm). This highlights the fact that DFT-derived adsorption energies alone are insufficient to explain the spatial distribution of methoxy adsorbates. Rather, the agreement between the simulation and experiment underscores the importance of applying the random-walk model assuming a Boltzmann distribution, which accounts for the thermal mobility and kinetic accessibility of the adsorbate configurations at room temperature.

4. CONCLUSIONS

The distribution and adsorbate–adsorbate interactions of methoxy adsorbates on the Pt/TiO₂(110) surface at room temperature were elucidated from their STM images. Applying TDA with PH to the STM images enabled the selective detection of the location of each methoxy adsorbate. The 2D auto-correlation function clearly shows the presence of repulsive interactions between neighboring methoxy adsorbates along the [001] direction of the TiO₂(110) surface. DFT calculations indicated that the repulsive interactions originated from steric hindrance between adjacent methoxy groups and electrostatic repulsion between the neighboring methoxy adsorbates. A Monte Carlo simulation using a 1D random walk model, which assumed a Boltzmann distribution, reproduced the distribution pattern of the methoxy adsorbates along the [001] direction. Our methodology, which combines topological, statistical, and computational methods, is effective for visualizing and understanding adsorbate–adsorbate interactions from STM images, even in the absence of long-range order, and can be applied to various adsorbate systems.

ASSOCIATED CONTENT

Supporting Information. Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

- Details of persistent homology analysis with superlevel set method for detection of the methoxy species, Plot of the E_{int} values as a function of the separation distance (d) between the two methoxy species and fitting with a power function

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) White, J. M.; Akhter, S. Adsorbate-Adsorbate Interactions during Coadsorption on Metals. *Crit. Rev. Solid State Mater. Sci.* **1988**, *14* (2), 131–173. <https://doi.org/10.1080/10408438808242182>.

- (2) Marshall, S. T.; Medlin, J. W. Surface-Level Mechanistic Studies of Adsorbate–Adsorbate Interactions in Heterogeneous Catalysis by Metals. *Surf. Sci. Rep.* **2011**, *66* (5), 173–184. <https://doi.org/10.1016/j.surfrep.2011.03.001>.
- (3) Lin, Y.-H.; Jeng, H.-T.; Lin, D.-S. Separation of the attractive and repulsive contributions to the adsorbate–adsorbate interactions of polar adsorbates on Si(100). *Surf. Sci.* **2015**, *641*, 282–288. <https://doi.org/10.1016/j.susc.2014.12.002>
- (4) Einstein, T. L. Interactions Between Adsorbate Particles. In *Handbook of Surface Science*, Vol. 1; Unertl, W. N., Ed.; Elsevier: Amsterdam, 1996; Chapter 11, pp. 577–650. [https://doi.org/10.1016/S1573-4331\(96\)80016-3](https://doi.org/10.1016/S1573-4331(96)80016-3)
- (5) Israelachvili, J. N. Classification of Forces and Pair Potentials. In *Intermolecular and Surface Forces*, 3rd ed.; Academic Press (Elsevier): 2011; Chapter 2.7, pp. 34–36. <https://doi.org/10.1016/C2009-0-21560-1>
- (6) Xia, S.; Wang, T.; Ren, Z.; Yang, X.; Guo, Q.; Zhou, C. Adsorption Structure–Activity Correlation in the Photocatalytic Chemistry of Methanol and Water on TiO₂(110). *Acc. Chem. Res.* **2024**, *57* (23), 3407–3418. <https://doi.org/10.1021/acs.accounts.4c00578>.
- (7) Zhang, R.; Luo, T.; Zeng, W.-W.; Zhou, C.; Yang, X.; Ren, Z. Methanol Adsorption and Reaction on TiO₂(110) at Near Ambient Pressure. *J. Phys. Chem. C* **2023**, *127* (2), 1049–1056. <https://doi.org/10.1021/acs.jpcc.2c08126>.
- (8) Shen, M.; Acharya, D. P.; Dohnálek, Z.; Henderson, M. A. Importance of Diffusion in Methanol Photochemistry on TiO₂(110). *J. Phys. Chem. C* **2012**, *116* (48), 25465–25469. <https://doi.org/10.1021/jp309768b>.
- (9) Zheng, Q.; Tan, S.; Feng, H.; Cui, X.; Zhao, J.; Wang, B. Dynamic Equilibrium of Reversible Reactions and Migration of Hydrogen Atoms Mediated by Diffusive Methanol on

Rutile TiO₂(110)-(1×1) Surface. *J. Phys. Chem. C* **2016**, *120* (14), 7728–7735.
<https://doi.org/10.1021/acs.jpcc.6b02367>.

(10) A. Henderson, M.; Otero-Tapia, S.; E. Castro, M. The Chemistry of Methanol on the TiO₂(110) Surface: The Influence of Vacancies and Coadsorbed Species. *Faraday Discuss.* **1999**, *114* (0), 313–329. <https://doi.org/10.1039/A902070E>.

(11) Silber, D.; Kowalski, P. M.; Traeger, F.; Buchholz, M.; Bebensee, F.; Meyer, B.; Wöll, C. Adsorbate-Induced Lifting of Substrate Relaxation Is a General Mechanism Governing Titania Surface Chemistry. *Nat. Commun.* **2016**, *7* (1), 12888.
<https://doi.org/10.1038/ncomms12888>.

(12) Sun, K.; Su, H.-Y.; Li, W.-X. Structures and Stability of Adsorbed Methanol on TiO₂(110) Surface Studied by Ab Initio Thermodynamics and Kinetic Monte Carlo Simulation. *Theor. Chem. Acc.* **2018**, *137* (10), 128. <https://doi.org/10.1007/s00214-018-2318-9>.

(13) Zhang, Z.; Bondarchuk, O.; White, J. M.; Kay, B. D.; Dohnálek, Z. Imaging Adsorbate O–H Bond Cleavage: Methanol on TiO₂(110). *J. Am. Chem. Soc.* **2006**, *128* (13), 4198–4199.
<https://doi.org/10.1021/ja058466a>.

(14) Phillips, K. R.; Jensen, S. C.; Baron, M.; Li, S.-C.; Friend, C. M. Sequential Photo-Oxidation of Methanol to Methyl Formate on TiO₂(110). *J. Am. Chem. Soc.* **2013**, *135* (2), 574–577. <https://doi.org/10.1021/ja3106797>.

(15) Takakusagi, S.; Fukui, K.; Tero, R.; Asakura, K.; Iwasawa, Y. First Direct Visualization of Spillover Species Emitted from Pt Nanoparticles. *Langmuir* **2010**, *26* (21), 16392–16396.
<https://doi.org/10.1021/la102013a>.

(16) Liu, C.; Lu, B.; Ariga-Miwa, H.; Ogura, S.; Ozawa, T.; Fukutani, K.; Gao, M.; Hasegawa, J.; Shimizu, K.; Asakura, K.; *et al.* Dynamic Behavior of Intermediate Adsorbates

to Control Activity and Product Selectivity in Heterogeneous Catalysis: Methanol Decomposition on Pt/TiO₂(110). *J. Am. Chem. Soc.* **2023**, *145* (36), 19953–19960. <https://doi.org/10.1021/jacs.3c06405>.

(17) Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum.* **2007**, *78* (1), 013705. <https://doi.org/10.1063/1.2432410>.

(18) Nečas, D.; Klapetek, P. Gwyddion: An Open-Source Software for SPM Data Analysis. *Open Phys.* **2012**, *10* (1), 181–188. <https://doi.org/doi:10.2478/s11534-011-0096-2>.

(19) Buchet, M.; Hiraoka, Y.; Obayashi, I. Persistent Homology and Materials Informatics. In *Nanoinformatics*; Tanaka, I., Ed.; Springer Singapore: Singapore, 2018; pp 75–95. https://doi.org/10.1007/978-981-10-7617-6_5.

(20) Obayashi, I.; Hiraoka, Y.; Kimura, M. Persistence Diagrams with Linear Machine Learning Models. *J. Appl. Comput. Topol.* **2018**, *1*, 421–449. <https://doi.org/10.1007/s41468-018-0013-5>.

(21) Gutierrez, A.; Buchet, M.; Clair, S. Persistent Homology to Quantify the Quality of Surface-Supported Covalent Networks. *ChemPhysChem* **2019**, *20* (18), 2286–2291. <https://doi.org/10.1002/cphc.201900257>.

(22) Kimura, M.; Obayashi, I.; Takeichi, Y.; Murao, R.; Hiraoka, Y. Non-Empirical Identification of Trigger Sites in Heterogeneous Processes Using Persistent Homology. *Sci. Rep.* **2018**, *8*, 3553. <https://doi.org/10.1038/s41598-018-21867-z>.

(23) Nakamura, R.; Ohashi, N.; Imanishi, A.; Osawa, T.; Matsumoto, Y.; Koinuma, H.; Nakato, Y. Crystal-Face Dependences of Surface Band Edges and Hole Reactivity, Revealed

by Preparation of Essentially Atomically Smooth and Stable (110) and (100) n-TiO₂ (Rutile) Surfaces. *J. Phys. Chem. B* **2005**, *109* (5), 1648–1651. <https://doi.org/10.1021/jp044710t>.

(24) Yamamoto, Y.; Nakajima, K.; Ohsawa, T.; Matsumoto, Y.; Koinuma, H. Preparation of Atomically Smooth TiO₂ Single Crystal Surfaces and Their Photochemical Property. *Jpn. J. Appl. Phys.* **2005**, *44* (4L), L511. <https://doi.org/10.1143/JJAP.44.L511>.

(25) van Dijk, N. P.; Maute, K.; Langelaar, M.; van Keulen, F. Level-Set Methods for Structural Topology Optimization: A Review. *Struct. Multidiscip. Optim.* **2013**, *48*, 437–472. <https://doi.org/10.1007/s00158-014-1145-4>.

(26) Obayashi, I.; Nakamura, T.; Hiraoka, Y. Persistent Homology Analysis for Materials Research and Persistent Homology Software: HomCloud. *J. Phys. Soc. Jpn.* **2022**, *91* (9), 091013. <https://doi.org/10.7566/JPSJ.91.091013>.

(27) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal--Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49* (20), 14251–14269. <https://doi.org/10.1103/PhysRevB.49.14251>.

(28) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561. <https://doi.org/10.1103/PhysRevB.47.558>.

(29) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6* (1), 15–50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).

(30) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54* (16), 11169–11186. <https://doi.org/10.1103/PhysRevB.54.11169>.

- (31) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953–17979. <https://doi.org/10.1103/PhysRevB.50.17953>.
- (32) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (33) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78* (7), 1396–1396. <https://doi.org/10.1103/PhysRevLett.78.1396>.
- (34) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104. <https://doi.org/10.1063/1.3382344>.
- (35) Diebold, U.; Hebenstreit, W.; Leonardelli, G.; Schmid, M.; Varga, P. High Transient Mobility of Chlorine on TiO₂(110): Evidence for “Cannon-Ball” Trajectories of Hot Adsorbates. *Phys Rev Lett* **1998**, *81* (2), 405–408. <https://doi.org/10.1103/PhysRevLett.81.405>.
- (36) Onishi, H.; Fukui, K.; Iwasawa, Y. Space-Correlation Analysis of Formate Ions Adsorbed on TiO₂(110). *Jpn. J. Appl. Phys.* **1999**, *38* (6S), 3830. <https://doi.org/10.1143/JJAP.38.3830>.
- (37) Ikeda, M.; Koide, N.; Han, L.; Pang, C. L.; Sasahara, A.; Onishi, H. Lateral Distribution of N3 Dye Molecules on TiO₂(110) Surface. *J. Photochem. Photobiol. Chem.* **2009**, *202* (2), 185–190. <https://doi.org/10.1016/j.jphotochem.2008.12.005>.
- (38) Hansen, S. I.; Sjølin, B. H.; Castelli, I. E.; Vegge, T.; Jensen, A. D.; Christense, J. M. An Adsorption Isotherm That Includes the Interactions between Adsorbates. *J. Phys. Chem. C* **2025**, *129*, 5393–5407. <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c08754>

(39) Onishi, H.; Iwasawa, Y. STM-Imaging of Formate Intermediates Adsorbed on a TiO₂(110) Surface. *Chem. Phys. Lett.* **1994**, 226 (1), 111–114. [https://doi.org/10.1016/0009-2614\(94\)00712-8](https://doi.org/10.1016/0009-2614(94)00712-8).

(40) Benziger, J. B. Influence of Dipole Interactions on Surface Reactions. *J Chem Soc Faraday Trans 1* **1980**, 76 (0), 49–59. <https://doi.org/10.1039/F19807600049>.

TOC Graphic

