Adsorption of Formic Acid on the Fe_3O_4 (001) Surface

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ABSTRACT

The adsorption of formic acid (HCOOH) on the Fe₃O₄(001) surface was studied using X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). At room temperature HCOOH dissociates to form formate (HCOO⁻) and hydroxyl groups, facilitated by the close proximity of undercoordinated Fe³⁺/O²⁻ cation/anion pairs at the Fe₃O₄(001) surface. Bidentate formate species are observed in IRRAS and their position on Fe-Fe bridge sites can be inferred from STM data. At 70 K, HCOOH is adsorbed both dissociatively and molecularly suggesting two active sites for dissociation. Our study also demonstrates that IRRAS is possible on Fe₃O₄ single crystals with good sensitivity, but that unusual peak shapes occur because the substrate is midway between a perfect conductor and a perfect dielectric.

KEYWORDS oxide surfaces, magnetite, acid-base, formic acid, adsorption

INTRODUCTION

The interaction of organic molecules with metal oxide surfaces is important in many areas including catalysis, corrosion, geochemistry, and environmental science. Formic acid (HCOOH), the simplest carboxylic acid is often used as a probe molecule to investigate the reactivity of metal-oxide surfaces. Adsorption can be molecular, particularly at low temperature, but is often dissociative on surfaces that expose under-coordinated cation/anion pairs (e.g. rutile-TiO₂(110) ¹⁻², MgO(100) ³, NiO(111) ⁴ CeO₂ ⁵, anatase-TiO₂(101) ⁶, ZnO ⁷, and SnO₂(110) ⁸). Such dissociation is typically described in terms of an acid-base reaction; the acidic proton of the HCOOH is abstracted by a basic O²⁻ anion, forming a O_{lattice}H species, while the remainder of the molecule, a formate (HCOO⁻) species, is bound to acidic metal cation sites ⁹:

Whether HCOOH dissociates upon adsorption on a metal-oxide surface depends on the atomic-scale structure; the cation/anion pair must be close enough together to facilitate the H transfer, while the degree of coordinative unsaturation (CUS) of the surface sites, i.e. the number of bonds missing in comparison to the bulk environment, affects the strength of the interaction ¹⁰. For this reason, step edges and point defects are typically more reactive than regular terrace sites.

On the Fe₃O₄(111) surface, HCOOH adsorption varies with the termination; dissociation occurs on a surface terminated by 1/4 ML Fe_{tet} atoms ¹¹, whereas molecular adsorption occurs on two other terminations ¹¹. The terminations often coexist and the structure of each remains somewhat controversial ¹², so it is difficult to draw further conclusions. The (001) surface, in contrast, undergoes a ($\sqrt{2} \times \sqrt{2}$)R45° reconstruction that dominates over a

wide range of chemical potentials ¹³⁻¹⁶. The reconstruction is linked to a rearrangement in the subsurface, but the surface layer is essentially bulk-like save for a subtle distortion of the lattice and the fact that all surface cations are Fe³⁺ ¹³. The surface has been shown to dissociate water at room temperature ¹⁷⁻¹⁹; here we turn our attention to the adsorption of an organic molecule, HCOOH. Our study is relevant for catalysis, as Fe₃O₄ is utilized as a catalyst for the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$), where formate has been proposed as a reaction intermediate ²⁰⁻²². Our fundamental study could also be of more general interest, e.g., in geochemistry since Fe₃O₄ (magnetite) is an abundant mineral in the Earth's crust.

EXPERIMENTAL METHODS

Room-temperature scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) experiments were conducted in an ultrahigh vacuum (UHV) system with a base pressure of 1×10^{-10} mbar. The STM measurements were performed at room temperature using an Omicron UHV-STM-1 instrument in constant current mode with electrochemically etched tungsten tips. XPS measurements were performed in two independent setups. First, measurements were performed in the STM chamber using Al K α x-rays and a SPECS PHOIBOS 100 analyzer at normal emission with pass energy 50 eV (not shown). Higher resolution, but otherwise similar XPS data were subsequently acquired in a second vacuum system (base pressure 1×10^{-10} mbar) using a SPECS FOCUS 500 monochromatic source and a SPECS PHOIBOS 150 electron analyzer at normal emission with a pass energy of 18 eV. In the second system, which also contains a commercial low-energy electron diffraction (LEED) setup, the sample could be cooled to 70 K using a Janis liquid He cryostat. IRRAS measurements were performed in a third UHV-system equipped

with an IR spectrometer Bruker Vertex 80v (Bruker Optics, Ettlingen, Germany) coupled to the UHV chamber via differentially pumped KBr-windows. Each IR spectrum was accumulated in 1024 Scans with a resolution of 2 cm^{-1} and was taken with the unpolarized beam at an incidence angle of 80° at a base pressure of 5×10^{-10} mbar.

Natural $\text{Fe}_3\text{O}_4(001)$ samples (SurfaceNet GmbH) were cleaned by 1 keV Ar^+ sputtering at room temperature for 20 minutes and then annealed in UHV at 873 K for 15 minutes. Prior to each experiment, the clean sample was annealed in O_2 (5×10^{-7} mbar) at 873 K for 15 minutes, which results in the growth of a virgin $\text{Fe}_3\text{O}_4(001)$ surface as excess Fe from the bulk is oxidized at the surface²³. HCOOH , obtained from Sigma Aldrich at a purity of 99.9 %, was purified with several freeze-pump-thaw cycles. For the STM and IRRAS experiments the gas was dosed into the background in the chamber through a high-precision leak valve. For the XPS and LEED experiments dosing was performed with an effusive molecular beam source. The XPS peaks were analysed with the CasaXPS program and fitted after subtraction of a Shirley background.

RESULTS

X-ray Photoelectron Spectroscopy

XPS measurements were conducted at room temperature and 70 K as a function of HCOOH exposure (Fig. 1). The C1s region has no detectable C signal when the surface is freshly prepared, but a peak emerges at 288.7 eV as the exposure is increased. At room temperature (Fig. 1a), the saturation coverage is obtained following a nominal exposure of 1.2 L, and the line shape is well approximated by two peaks; a major contribution at 288.7 eV and a smaller shoulder at 289.8 eV (Fig. 1c). The peak at 288.7 eV is consistent with adsorbed formate, which typically appears below 289 eV on other metal-oxide surfaces^{3, 24-}

²⁵. The shoulder at 289.8 eV is more typical of undissociated HCOOH. In the O1s region (Fig. 1b), the clean Fe₃O₄(001) surface exhibits a slightly asymmetric peak at 530.1 eV, as reported previously ²⁶. As HCOOH is deposited this peak decreases in intensity and a shoulder emerges on the high-energy side (at approximately 532.2 eV) which gets saturated by 1.2 L. This position of this peak is consistent with both OH groups and formate species on other metal-oxide surfaces ^{24-25, 27}. Fig. 1d shows a direct comparison of the clean surface and 5L HCOOH O1s data.

When the same experiment is performed with the sample at 70 K, the C1s data closely resembles that acquired at room temperature at low exposure (≤ 0.4 L), exhibiting a single peak at 288.7 eV (Fig. 1e). As the exposure is increased however, the peak broadens and shifts toward higher binding energy. At 1.2 L, the peak area is close to that obtained for the corresponding exposure at room temperature data, and the spectrum can be fit by two components at 288.7 eV and 289.7 eV (Fig. 1g). When the exposure is increased further, the peak at 289.7 eV grows without saturation, consistent with the condensation of HCOOH multilayers onto the sample. In O1s (Fig. 1f), a shoulder again emerges on the high binding-energy side, but its intensity continues to grow with increasing exposure, as expected for HCOOH multilayers. A direct comparison of the data with the Fe₃O₄(001) surface before and after exposure to 5 L HCOOH (Fig. 1h) shows the peak related to the substrate is more greatly diminished by the HCOOH multilayers than it was by the formate monolayer in Fig. 1d. XPS scans of the C1s region performed following stepwise annealing of the HCOOH exposed sample show that spectra resembling the clean Fe₃O₄(001) surface are recovered at ~ 473 K (not shown).

Figure 1. C1s and O1s XPS spectra following exposure of the $\text{Fe}_3\text{O}_4(001)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ surface to HCOOH at room temperature (left) and 70 K (right). The upper panels show the evolution of the XPS spectra as a function of HCOOH exposure. The bottom panels show best fit of the C1s data, for 5 L exposure at room temperature, and 1.2 L at 70 K. For the O1s data, a direct comparison of the clean and 5 L data is shown in each case.

Infrared reflection absorption spectroscopy

To shed further light on the nature of the adsorbed species we performed IRRAS experiments. Fe_3O_4 is neither a perfect conductor (metal), the usual substrate for IRRAS experiments on single-crystal surfaces, nor a perfect dielectric, as typical for IRRAS experiments on oxide single crystals performed so far (e.g., Refs. ²⁸⁻²⁹). It has been noted earlier that asymmetric peaks or Fano lineshapes can occur for poorly conducting substrates ³⁰⁻³¹, and it is also unexplored so far whether IRRAS shows reasonable sensitivity for adsorbates on such a substrate. We therefore start by calculating the expected line shape and strength for adsorbates with vertical dipole moment on Fe_3O_4 in comparison to that on a metal [Fig. 2(a)]. The calculations are based on equation (6) from Ref. 30, where the fractional change in reflectivity ($\Delta R/R$) is given by

$$\frac{\Delta R}{R} = -32\pi^2\nu \frac{\sin^2\theta}{\cos\theta} [\text{Re}(\beta)\text{Im}(N_s\alpha) + \text{Im}(\beta)\text{Re}(N_s\alpha)] \quad (2).$$

Here

$$\alpha = \alpha_e + \frac{\alpha_v}{1 - (\nu/\nu_0)(\nu/\nu_0 + i\gamma/\nu_0)}, \quad (3)$$

is the polarizability of the adsorbate, where α_e is the frequency-independent electronic polarizability, α_v is the vibrational polarizability, ν is the frequency of the light, ν_0 is the resonant frequency and γ is the linewidth.

$$\beta = \frac{1}{(1 - 1/\epsilon)(1 - \tan^2\theta/\epsilon)} \quad (4),$$

where ϵ is the complex dielectric function of the material. For the plot in Fig. 2 we choose θ as the experimental angle of incidence (80°). The density of adsorbates N_s and α_v

determine the peak height and were chosen arbitrarily, only ensuring that $\Delta R/R$ is small; α_e can be neglected. For the real and imaginary components of the dielectric function for Fe_3O_4 we use $\text{Re}(\epsilon) = 13$ and $\text{Im}(\epsilon) = 10$, from Ref. 32. For the metallic comparison, we use the values $\text{Re}(\epsilon) = -2000$ and $\text{Im}(\epsilon) = 260$, otherwise the same data as for the Fe_3O_4 substrate. This ϵ value is for Cu; but the result for the metallic substrate is insensitive to ϵ as long as $\text{Re}(\epsilon) < -500$.

Clearly, the absorption signal of Fe_3O_4 has a Fano-like shape with wings extending far to the left and right, but the peak-peak amplitude is similar to the peak height for the same adsorbate on Cu. For an almost antisymmetric peak shape, as in the current case, the point of maximum slope is close to the vibrational frequency of the molecule. Our calculations reveal that if $\text{Im}(\epsilon)$ is much less than $\text{Re}(\epsilon)$ the near-antisymmetric IRRAS peaks occur only in a very narrow region around the Brewster angle (Here, $\theta_B = 77^\circ$).

The experimental spectra are shown together with a spectrum of the clean sample taken before HCOOH was deposited. After dosing 2 Langmuir (L; $1 \text{ L} = 10^{-6} \text{ torr s}$) HCOOH at room temperature [Fig. 2(b)], a resonance at 1370 cm^{-1} appears and reaches saturation around a dose of 10 L. The peak shape agrees with the calculation for an out-of-plane dipole moment. In addition, a resonance with similar, but inverted shape appears at $\approx 1540 \text{ cm}^{-1}$; this indicates an in-plane dipole moment. These peak frequencies are characteristic for the symmetric (1370) and asymmetric (1540 cm^{-1}) OCO stretch of formate species³³⁻³⁵. Two additional features in Fig. 2(b) should be mentioned. The first is

a double positive peak for the 1370 cm^{-1} resonance, with absorption maxima very close to the steep slope ($\approx 1372\text{ cm}^{-1}$) and $\approx 1385\text{ cm}^{-1}$. This indicates the superposition of two resonances near 1370 cm^{-1} ; we attribute the weaker signal to the C-H bending mode $\delta(\text{CH})$. As it is superimposed on the strong symmetric OCO stretch signal, the position and shape of the weaker peak cannot be determined with any certainty. No bands are observed in the region around 1700 cm^{-1} , which would be expected for the $\nu(\text{C}=\text{O})$ stretch of intact HCOOH molecules³³⁻³⁵. Thus, the room-temperature spectra confirm the assignment of the XPS spectra to formate and show an upright (bidentate) orientation of the molecule. An OH stretch mode as expected on the basis of equation (1) was not detected, but OH has a small dynamic dipole moment, and was not observed on some other metal oxide surfaces either⁶. IRRAS data recorded at 190 K after exposure to HCOOH at the same temperature [Fig. 2(c)] show the symmetric and asymmetric OCO stretch signals at almost the same wavelengths (1365 and 1550 cm^{-1}). In addition, a broad peak appears at $\approx 1710\text{ cm}^{-1}$ which can be assigned to the stretching vibration mode of $\nu(\text{C}=\text{O})$ in molecularly adsorbed HCOOH ³³⁻³⁵. This nicely fits the observation of molecular HCOOH upon low-temperature adsorption in XPS.

Figure 2. IRRAS spectra (a) calculated for a resonating vertical dipole moment on Cu and Fe_3O_4 , and experimental spectra at (b) room temperature and (c) 190 K acquired for the clean $\text{Fe}_3\text{O}_4(001)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ surface and following exposure to 2 L and 10 L HCOOH . The asymmetric (1540 cm^{-1}) and symmetric (1370 cm^{-1}) vibration modes are sketched in small boxes. A linear background has been subtracted from the spectra in (c).

Low energy electron diffraction

The clean $\text{Fe}_3\text{O}_4(001)$ surface exhibits a $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ LEED pattern (Fig 3a) linked to a rearrangement of the cations in the surface layers¹³. When the surface is exposed to 5 L HCOOH at room temperature (i.e. the saturation exposure determined by XPS) the spots related to the $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ reconstruction disappear and the surface exhibits (1×1) periodicity (Fig. 3c). Since the half-order spots are absent at all energies, this observation implies that the $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ reconstruction is lifted by the dissociative adsorption of HCOOH . At 70 K however, following exposure to 1.2 L of HCOOH , close to saturation of the dissociated species according to XPS, the LEED pattern retains some intensity of the $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ superstructure (Fig. 3b).

Figure 3. LEED patterns acquired from the $\text{Fe}_3\text{O}_4(001)$ surface with an electron energy of 90 eV . (a) Clean surface. The yellow square shows the $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ periodicity of the surface reconstruction, whereas the green square indicates the (1×1) unit cell. (b) After

exposure to 1.2 L HCOOH at 70 K, the $(\sqrt{2}\times\sqrt{2})R45^\circ$ periodicity is maintained, although the spots are less intense than for the clean surface. (c) After exposure to 5 L HCOOH at room temperature, the spots associated with the $(\sqrt{2}\times\sqrt{2})R45^\circ$ are absent and the surface exhibits a (1×1) periodicity (green square).

Scanning tunneling microscopy

For the adsorption of HCOOH on $\text{Fe}_3\text{O}_4(001)$ at room temperature we performed STM measurements. STM images of the clean $\text{Fe}_3\text{O}_4(001)$ - $(\sqrt{2}\times\sqrt{2})R45^\circ$ surface are characterized by rows of protrusions separated by 5.9 Å, related to the surface Fe_{oct} atoms (Fig. 4a) ¹³. The row direction switches between [110] and [1-10] on neighboring terraces that are separated by a step of (2 Å) height; consistent with the inverse spinel structure of magnetite. The surface oxygen atoms of the $\text{Fe}_{\text{oct}}\text{-O}$ termination are not observed in STM because they have little density of states in the vicinity of E_F ³⁶. Various defects are observed on the as prepared surface including, antiphase domain boundaries in the surface reconstruction ³⁷, occasional Fe adatoms ¹⁵ and surface OH groups, which form through the dissociation of water from the residual gas at oxygen vacancies ¹⁹. Although the OH are not imaged directly, the neighboring Fe atom pairs are reduced and appear brighter in empty states STM images ²⁶.

Following a nominal exposure of 1L HCOOH (Fig. 4b), the Fe rows of the $\text{Fe}_3\text{O}_4(001)$ substrate are completely obscured. Patches of circular protrusions (apparent height 20 pm) are separated by areas characterized by streaks in the fast-scan direction of the STM (vertical in the image). Such streaks typically result from weakly bound molecules moving under the influence of the STM tip. The protrusions have a nearest neighbor distance of 5.9

Å in the [1-10] direction, which corresponds to every other Fe atom along the Fe_{oct} row. In some cases the nearest neighbor is 5.9 Å away in the [1-10] direction (yellow line joins two such protrusions), which corresponds to equivalent sites on the neighboring Fe row. In other areas neighboring protrusions are located 6.6 Å away at an angle $\pm 26.6^\circ$ from the [110] axis (orange line in Fig. 4b).

When the exposure is increased to 10 L HCOOH, the surface is covered by a nearly complete overlayer of protrusions (Fig. 4c). In some areas the protrusions are arranged with a square pattern with a nearest neighbor distance of 5.9 Å (one such patch is indicated by the yellow square); this corresponds to a (1×1) registry with the substrate. In other areas the protrusions are arranged with a local (2×1) order. This order is an extension of the 6.6 Å configuration observed in Fig 4b (orange rectangle). Occasionally, a row of protrusions running in the [110] direction exhibits a gap of 9 Å (red arrow), which results in a switch of the local ordering with the neighboring protrusions.

Figure 4. STM images of the clean $\text{Fe}_3\text{O}_4(001)$ surface and following exposure to HCOOH at room temperature. (a) The as-prepared $\text{Fe}_3\text{O}_4(001)$ surface ($20 \times 10 \text{ nm}^2$, $V_{\text{sample}} = 1.6 \text{ V}$, $I_{\text{tunnel}} = 0.1 \text{ nA}$). (b) After exposure to 1 L HCOOH , the surface is characterised by protrusions associated with formate species, and areas obscured by rapidly diffusing molecules ($20 \times 10 \text{ nm}^2$, $V_{\text{sample}} = 1.5 \text{ V}$, $I_{\text{tunnel}} = 0.1 \text{ nA}$). (Fast scan direction vertical.) (c) After dosing 10 L of HCOOH , close packed formate species cover the surface ($20 \times 10 \text{ nm}^2$, $V_{\text{sample}} = 1.5 \text{ V}$, $I_{\text{tunnel}} = 0.1 \text{ nA}$). Two local orderings of the protrusions are observed (1×1) (within the yellow square) and (2×1) (within the orange rectangle). The red arrow points to a $9 \text{ \AA}$ gap between protrusions in the $[110]$ direction, either side of which the local order switches between (1×1) and (2×1).

DISCUSSION

Like most metal oxides, Fe_3O_4 is characterized by a high degree of ionicity in the metal-oxygen bond. Consequently, the atoms are charged, and the reactivity of the surface can be understood in terms of acid-base reactions^{9, 38-39}. The XPS and IRRAS data presented here show that HCOOH is adsorbed dissociatively at room temperature to form formate, consistent with equation (1). Dissociation is facile in the system because the Fe^{3+} cations and O^{2-} anions are very close together on the surface (2 Å), which promotes an acid-base reaction. We propose that formate binds through the O atoms to two neighboring Fe atoms along the Fe_{oct} row in a bridging bidentate configuration. A similar adsorption geometry was recently measured on the $\text{TiO}_2(110)$ surface⁴⁰, and the Ti-Ti separation is similar to the Fe-Fe separation here (3 Å). Fig 5 shows a schematic representation of the ordering observed in STM (Figure 4c) superimposed on a $\text{Fe}_3\text{O}_4(001)-(1\times 1)$ surface (unit cell indicated by black square). The blue rectangles represent bridging bidentate formate bound to two surface Fe_{oct} atoms along the row between subsurface Fe_{tet} atoms. In the (1×1) ordered area formate binds to symmetrically equivalent Fe_{oct} pairs, but the (2×1) ordering formate requires that an inequivalent Fe_{oct} pair is occupied that straddles the line between two subsurface Fe_{tet} atoms (green). Note that in the centre of Fig. 5 one Fe_{oct} atom is not occupied by formate; this results in a distance of 9 Å between formate species along the row direction, as observed experimentally at the border between the (1×1) and (2×1) phases (Fig. 4).

Figure 5. Schematic model of bridging bidentate formate adsorption on a $\text{Fe}_3\text{O}_4(001)$ -(1 $\times$ 1) surface. Blue rectangles represent formate bound to an Fe_{oct} pair located in the center of four subsurface Fe_{tet} atoms (cyan), whereas green rectangles represent formate bound to an Fe_{oct} pair that straddles the line between two subsurface Fe_{tet} . While a (1 $\times$ 1) periodicity can be formed by either the green or blue formate, both configurations are required to form the (2 $\times$ 1) periodicity observed in STM.

The data acquired at low temperature show that both molecular and dissociative adsorption occurs. This suggests two barriers for HCOOH dissociation, the first being facile at 70 K and a second with higher activation energy. It seems likely that the first dissociation event in each $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ unit cell results in bridging bidentate formate, with an OH group formed at the O atoms without a subsurface Fe_{tet} neighbor. Preferential hydroxylation of these surface O sites has been observed for low coverages of atomic H²⁶, and following dissociative adsorption of H_2O ¹⁹. A second dissociation event per unit cell, which does not

occur at low temperature, is linked to the lifting of the $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstruction, as observed in LEED at room temperature. Lifting the reconstruction must involve the relocation of the 2nd layer interstitial Fe_{tet} atom that underlies the subsurface rearrangement¹³, so it is plausible that this process would require more thermal energy. Exactly how the second dissociation event causes the necessary rearrangement of the subsurface cations is not yet clear, but it appears to be linked to the adsorption of the second H atom. In this context it is important to note that a similar lifting of the $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstruction was previously reported following saturation exposure to atomic H²⁶, and exposure to water^{17,41}.

While the formate is clearly identified in the room temperature data, the OH species expected on the basis of equation (1) are not detected by IRRAS, imaged by STM, nor uniquely resolved in the O1s XPS spectrum. We note however that DFT calculations predict the OH bond to be parallel to the surface²⁶, which makes detection by IRRAS problematic. Also, the corrugation of the STM images is dominated by the formate species at high coverage, and the substrate is obscured by loosely bound HCOOH molecules already at low coverage. Finally, where we expect to find the OH peak in O1s XPS, we also find the formate peak which has double the intensity.

The reactivity of the Fe₃O₄(001) surface described above is in line with that observed for other metal-oxide surfaces. HCOOH dissociates at regular terrace sites of almost all metal-oxide surfaces at room temperature, with the only exception being surfaces which do not expose undercoordinated cation-anion pairs, such as the oxygen-terminated polar surfaces of ZnO(0001)¹⁰.

CONCLUSIONS

The interaction of formic acid (HCOOH) with Fe₃O₄ (001) surface was studied experimentally using XPS, IRRAS and STM. HCOOH dissociates at room temperature yielding a layer of bridging bidentate formate and surface hydroxyl groups. Partial dissociation at 70 K indicates two different active sites for adsorption. The results are in line with observations on other metal-oxide surfaces and can be understood in terms of acid-base chemistry.

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