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Anchoring of phthalic acid on MgO(100)^{\star}



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ABSTRACT

Carboxylic acids are often used to anchor large organic molecules to oxide surfaces. To understand the mechanism of this anchoring we have studied the temperature and coverage-dependent adsorption and reactions of phthalic acid on MgO(100) by a combination of X-ray photoelectron spectroscopy, near-edge X-ray absorption, UV photoelectron spectroscopy and density-functional theory. At 110 K, phthalic acid partly deprotonates on MgO(100) at low coverage and forms a dicarboxylate species. At higher coverage, the fraction of intact phthalic acid increases to a larger extent than that of the deprotonated species. Subsequent annealing of these mixed structures results in the full conversion of the remaining intact acid groups to carboxylate, that is, doubly deprotonated phthalic acid, at 250 K. Depending on coverage, the carboxylate-bonded species remain stable up to 500 – 600 K. Above this temperature, the molecules decompose and desorb as fragments, leaving only a small carbon residue behind on the surface.

1. INTRODUCTION

Motivated by growing concerns about global warming and the depletion of petroleum resources, developing renewable energy production, transportation and storage technologies is one of the major scientific challenges of the twenty-first century. Hybrid organic/inorganic materials are promising systems, because they combine the structural and chemical flexibility of organic molecules with the tunable electronic properties and durability of inorganic compounds. Examples, where hybrid materials have been used, include photovoltaic cells [1–3], organic electronics [4–6], fuel cells [7–10], advanced batteries [11–14] and supercapacitors [15–17]. In all these applications, the interface between the inorganic substrate and adsorbed organic molecules is critical for the performance of the device. Anchoring groups are one way of tuning the properties of the interface and are widely used for hybrid materials [18–25]. Linking a functional organic molecule to an inorganic substrate can, for instance, yield a more efficient charge transfer at the interface [26-28] or, alternatively, can be used to generate well-defined structures of supramolecular assemblies [29-31]. For large organic molecules, however, the interaction of the anchor groups with the surface is only one of many interactions determining the properties of the interface. Other interactions include saddle-shape deformation and T-type interactions in tetrapyrroles [32–34], π - π stacking in conjugated molecules [35,36] or the formation of two-dimensional networks with intermolecular hydrogen or coordination bonds [37–39].

In this study, we focus on the interaction of the anchor groups with the surface. We have therefore chosen a relatively small molecule, phthalic acid, see Fig. 1, where the dominant interaction is the interaction of the anchor groups with the surface. Phthalic acid has two neighboring carboxylic-acid anchor groups and can be seen as a model for molecules with multiple anchor groups. Multiple anchor groups make the adsorbed molecules more rigid, affecting the possible structures, but may also lead to more efficient charge transfer between the molecule and the surface [18]. Carboxylic acids often bind to oxide surfaces through the formation of carboxylates, where the oxygen atoms of the acid group bind to the cations in the oxide surface. The adsorption behavior therefore depends strongly on the density and accessibility of

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cations in the oxide surface [40], and, especially for molecules with multiple anchor groups, this leads to many possible binding motifs [21, 22,40-49], see Fig. 1.

An example, of how the structure of the surface can drastically affect the packing density, is the adsorption of terephthalic acid (two carboxyl groups located at the different sides of benzene ring) on rutile TiO₂(110): On the unreconstructed (1 \times 1) surface, the binding motif switches from flat-lying to upright-standing [46] with increasing coverage, whereas on the reconstructed (1 \times 2) surface the molecules adsorb upright-standing in between Ti₂O₃ strings leading to a two times lower saturation coverage as compared to the (1 \times 1) surface [42].

An example for the diversity of adsorption motifs is the adsorption of phthalic acid on cobalt oxide. On $Co_3O_4(111)$, at 130 K as well as at room temperature phthalic acid forms double chelating bidentate carboxylate bonds at submonolayer coverage, while at multilayer coverage a single chelating bidentate geometry is deduced for the first layer in contact with the substrate from infrared spectroscopy [40]. In contrast, on CoO(100) at 130 K the first layer of phthalic acid binds in a double-bridging bidentate geometry at submonolayer coverages and a single-bridging bidentate in the first layer at multilayer coverages [40]. CoO(111) tends to undergo a surface reconstruction upon annealing, and at 130 K submonolayer coverages of phthalic acid adsorb in the form of double-bridging bidentate species while at 300 K the binding motif changes to a mixed double-bridging bidentate/single chelating bidentate [40].

The adsorption geometry of phthalic acid on MgO(100) previously studied by IR spectroscopy [22] was found to be coverage-dependent, changing from a double bidentate carboxylate at submonolayer coverage to single bidentate carboxylate at multilayer coverage. The authors claim that these trends persist both at 100 and 300 K. Because of such a variety, binding motifs of organic molecules deposited on oxide surface can be accurately revealed only by a surface science approach. Herein, we provide a comprehensive atomic-scale understanding of phthalic acid (PA) adsorbed on the prototypical rock-salt oxide MgO(100) [50–62] using synchrotron-radiation X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS) and near-edge X-ray-absorption fine structure (NEXAFS), combined with density-functional theory (DFT). We will show how the binding motif of the molecule changes as a function of coverage and temperature. Our results can be used to better understand the behavior and properties of much larger functional organic molecules with carboxylic acid anchor groups.

2. Materials and methods

The experiments were performed at the Materials Science beamline at ELETTRA Synchrotron, Trieste. Normal-emission XP spectra were acquired using a SPECS Phoibos 150 electron energy analyzer. All spectra were normalized to the photon flux, measured by photocurrent passing through a gold mesh installed in the beamline. The base pressure in the measuring chamber was below 5×10^{-10} mbar.

To avoid charging effects in XPS associated with the isolating properties of bulk MgO, we worked with thin films of MgO(100) grown on a Ag(100) single crystal (Surface Preparation Laboratory). The crystal was cleaned by repeated cycles of 30 min Ar⁺ sputtering at 0.8 keV and 25 μ A, and annealing at 700 K for 20 min. MgO(100) thin films with thicknesses from 6 to 8 ML, as estimated from XPS, were prepared using recipes from literature [63] by evaporating Mg from a stainless steel crucible (kept at 630 K) onto the Ag(100) substrate held at 450 K in 1×10^{-6} mbar of O₂. The films were subsequently annealed to 650 K in 1×10^{-6} mbar O₂ for 5 min to improve their crystallinity, and their (1 \times 1) structure was confirmed by LEED (Figure SI 1). The purity of the films was checked with XPS, yielding a remaining carbon contamination of ~3 at.%. Phthalic acid (Sigma-Aldrich, \geq 99.5%) was evaporated from a graphite crucible held at 400 K. For performing heating series,



Fig. 1. Schematic illustrations of the different binding geometries of carboxylic acid (top row) and phthalic acid (middle and bottom row) discussed in the text.

the temperature was monitored by K-type thermocouple directly attached to the Ag(100) sample.

Coverages of phthalic acid on MgO were calculated using Eq. (1) [64] taking into account that the photoemission lines were measured at the same kinetic energies of 100 eV:

$$h = \lambda \cdot \ln \left(I_{C/Mg} \middle/ I_{C/Mg}^0 + 1 \right) \tag{1}$$

where $I_{C/Mg}$ is the ratio of the C 1s and Mg 2p signals, $I_{C/Mg}^0$ is the ratio of the C 1s signal from an infinitely thick phthalic acid film and the Mg 2p signal from a clean MgO surface, *h* is the thickness of the film, and λ is the inelastic mean free path of the C 1s and Mg 2p photoelectrons measured at the same kinetic energy. The C 1s intensity from a sufficiently thick layer of phthalic acid molecules such that the Mg 2p signal has completely vanished was used as reference for an infinitely thick phthalic acid film. Lastly, to determine the inelastic mean free path we used the phthalic acid monolayer left on the surface after annealing to 300 K and above as a reference for a thin even film with a coverage we define to be one monolayer. Because of the low inelastic mean free path at a kinetic energy of 100 eV the MgO(100) films were thick enough to completely attenuate the signal from the Ag(100) substrate. This allowed us to treat the MgO(100) thin films as being infinitely thick for coverage-calculation purposes.

Coverages for MgO on Ag(100) were calculated from photoemission spectra acquired with an Al K α source, producing photoelectrons with the higher kinetic energies needed to penetrate the MgO(100) films. The calculations were done using Eq. (2) and assuming that the intensity of the substrate follows a simple exponential decay law [64]:

$$I_{Ag} = I_{Ag}^{0} \cdot \exp\left(-h \left/ \lambda_{Ag}\right)$$
⁽²⁾

where I_{Ag} is the attenuated Ag 3d signal from the Ag(100) substrate, I_{Ag}^0 is the Ag 3d signal from a clean substrate, *h* is the thickness of the film and λ_{Ag} is the inelastic mean free path of the Ag 3d photoelectrons travelling through the MgO film calculated from the Tanuma-Powel-Penn formula [65,66].

NEXAFS spectra were acquired following the C KLL or O KLL Auger peak intensity. Grazing and normal incidence spectra were measured at 80° incidence / 20° emission and 0° incidence / 60° emission relative to the surface normal, respectively. The usual normalization to the photon flux provided by the photocurrent measured at the gold mesh was not possible for the C K-edge absorption spectra due to the contamination of the X-ray optical elements of the beamline. Therefore, the photon flux was calculated by measuring the Mg 2p peak of the MgO(100) surface in the same photon energy range (277-320 eV). Afterwards, the C K-edge spectra were normalized with the obtained photon flux. The NEXAFS spectra measured by this method contain not just the desired Auger peaks, but also photoemission features traveling through the Auger spectra, which severely complicates data analysis. To eliminate these photoemission features, we used a very efficient clean-up procedure developed by Lytken and co-workers Ref. [67]. The procedure describes the measured image as three simple, one-dimensional spectra, namely NEXAFS, Auger and XP spectra. This simple description allows for removing photoemission features without any reference measurements other than the photon flux.

Ab-initio DFT calculations were performed using the VASP package (Version 6.1.1) [68–70] with the PBE exchange-correlation functional [71]. The projector augmented wave method (PAW) [72] was used to take into account the core electrons. An energy cutoff of 450 eV was chosen for the plane wave basis. To describe the long-range London dispersion interactions the new correction scheme DFT-D4 [73,74] by Grimme and coworkers, which additionally takes into account the atomic charges, was applied. A Methfessel-Paxton [75] smearing with a broadening of 0.1 eV was included. A supercell approach with a six layer slab of MgO was used to model the systems, including a 20 Å layer of vacuum separating the periodic images in *z*-direction. For magnesium

oxide, a lattice parameter of 4.26 Å was used. The three bottom layers were fixed to the bulk geometry during the optimizations while the top three layers were relaxed. The geometry was optimized until all forces were smaller than 0.01 eV/Å. The model for low coverage consists of a 3×3 conventional MgO unit cell with a single molecule of phthalic acid and was calculated with a $4 \times 4 \times 1$ Gamma centered Monkhorst-Pack [76] k-point mesh. This geometry was obtained, starting from the already published "Geometry A" in the study by Xu et al. [22]. For higher coverages a 3 \times 4 unit cell was used with a k-point mesh of 4 \times 3 \times 1 k-points. In this cell 4 PA molecules were added. Additionally, calculations with an underlying silver substrate were performed due to an improved behavior of calculations of core level shifts. For these calculations, 6 layers of a Ag(100) surface with a lattice constant of 4.26 Å, compatible to the MgO, were added. In a first step, the interface was relaxed with the bottom three layers of the silver being fixed, while the three remaining layers of silver and all six MgO layers were optimized. For the adsorption studies, the bottom 9 layers, including the interface were fixed and only the three topmost MgO layers were allowed to relax. Adsorption energies E_{ads} were calculated as total energy differences between the clean surface unit cell E_{surf} plus the energy of the molecule in gas phase E_{mol} minus the total energy of the combined system E_{svs} as $E_{ads} = E_{mol} + E_{surf} - E_{sys}$. Therefore, higher adsorption energies correspond to higher stability. To gain further insight into experimental XP spectra, core level shifts were calculated by relative core electron binding energies with the method of Slater's transition state [77] (ICORELEVEL=2, CLZ=0.5) removing half an electron.

3. Results and discussion

3.1. Coverage- and temperature-dependent reactivity of phthalic acid adsorbed on MgO(100)

3.1.1. Temperature-dependent reactivity of phthalic acid multilayers

We start probing the structure and reactivity of phthalic acid multilayers adsorbed on the MgO(100) surface. Fig. 2 shows the O 1s, Mg 2p and C 1s XP spectra acquired after deposition of 2.3 ML phthalic acid onto a 7.5 ML MgO(100) thin film grown on a Ag(100) single crystal (see details in Material and Methods section), followed by heating to 650 K. For comparison, the spectra of phthalic acid multilayers (> 6 ML) on Ag(100) and the spectra of clean MgO(100) are shown at the top and the bottom of the Fig. 2, respectively. 1 ML of phthalic acid on the MgO(100) film is defined as the coverage of the stable structure formed at 300-550 K after the multilayers have desorbed (see Materials and Methods section for details). The quantitative analysis of the data in Fig. 2 is depicted in Fig. 3 together with the ratio of the O 1s to the C 1s peak areas of the carboxylic acid-related signals calculated as sum of the components (C=O + C-OH + C-O-Mg) in O 1s spectra divided by the sum of the components (O-C=O + C-O-Mg) in C 1s spectra. Three different temperature regions can be identified in Figs. 2 and 3 corresponding to the different stable species related to phthalic acid: 110 - 150 K, 300 - 550 K, and 650 K. Between these temperatures pronounced changes occur.

From 110 - 150 K intact multilayers of phthalic acid are observed. Because of the strong photoelectron attenuation (50% per ML) no conclusions about the state of the first layer in contact with the MgO(100) surface can be made based on this spectrum. The presence of intact carboxylic acid groups is confirmed by two characteristic features in the O 1s spectrum in Fig. 2, namely the C–OH located at 533.7 eV (violet) [^{41, 44, 45]} and the C=O at 532.6 eV (violet) [^{41, 44, 45]}, with a 1:1 ratio, as expected for the intact molecules. This corresponds well to the XP spectra calculated with DFT for an isolated PA trimer structure (Fig. 4, topmost spectrum, and SI 3). The two components in the C 1s spectra are assigned to the benzene ring (285.6 eV; green) and the carboxyl groups (289.8 eV, violet), [41,43-45] further corroborating the presence of intact phthalic acid. The small additional feature at 291.9 eV corresponds to the $\pi \rightarrow \pi^*$ shake-up satellite of the aromatic system [78,79]. The O/C ratio of the components of the carboxylic acid group in this



2.3 ML Phthalic acid/MgO(100)

Fig. 2. O 1s (left), C 1s (center) and Mg 2p (right) XP spectra of 2.3 ML of phthalic acid deposited on MgO(100) substrate followed by stepwise annealing. XP spectra were measured at high surface sensitivity with an electron kinetic energy of 100 eV for each core level, by using photon energies of 160 eV for the Mg 2p, 380 eV for the C 1s, and 650 eV for the O 1s regions. Dots show experimental data, while solid lines represent fitted curves.

temperature is \sim 2.6 (Fig. 3b, red squares) which is somewhat larger than the expected value of 2.0. This may be due to the presence of co-adsorbed water, which would result in an O 1s XPS peak at around 534 eV [80] overlapping with the C–OH signal.

Annealing of the phthalic acid multilayers to 300 K leads to desorption of the multilayer, as seen by the coverage decrease in Fig. 3a. The remaining saturation coverage of 1 ML in the temperature range 300 - 550 K is indicated as dashed horizontal line in Fig. 3a. Multilayer desorption goes along with a gradual transformation to a new state, which is stable in the range 300 - 550 K. This state is characterized by a new single component in the O 1s spectrum at 532.1 eV (orange), the disappearance of the C-OH component at 533.7 eV in the O 1s spectrum at 289.3 eV (orange). The appearance of only one new component in the

O 1s spectra indicates only one type of oxygen atoms in the formed species. This rules out adsorption structures with only a single carboxylate bond to the surface (Fig. 1, g-l) and implies that all species are doubly deprotonated, leaving double bidentate structures as only possible motifs (Fig. 1, e,f). Also note that water molecules present in the multilayer are expected to desorb by 250 K [81]. The formation of the new species is accompanied by an increase of the ratio of the O 1s and the C 1s areas in the carboxylic group to 3.3:1 in Fig. 3b. This ratio is larger than the expected 2:1 ratio as deprotonation of the C–OH group results in the formation of surface hydroxyl groups, which give an O 1s peak at around 532 eV [80] overlapping with the C-O-Mg signals. Note that a doubly deprotonated molecule results in two surface hydroxyl groups, thus the expected O/C ratio would be 3:1 as observed. Thus from the O 1s/C 1s ratio we also conclude that both carboxylic acid groups of



Fig. 3. (a) Film thicknesses for 2.3 ML (orange) and 0.4 ML (blue) of phthalic acid deposited on MgO(100) substrate calculated using Eq. (1) plotted as a function of temperature. Dashed line indicates 1 ML determined as saturation coverage of phthalic acid remaining on the surface after multilayer desorption at 300 K. Dotted line represents average thickness for the submonolayer sample. (b) atomic ratio of O to C in carboxylic acid groups calculated based on area of components in the corresponding O 1s and C 1s photoemission spectra.

phthalic acid are deprotonated at this stage.

The chemical nature of the new state can be further analyzed by correlating the XPS data with the possible binding configurations of phthalic acid on the oxide surface determined by our DFT calculations. For this reason, various structures have been investigated, starting from different binding motifs, different surface coverages, and by further refining the most promising structures. In Fig. 5, the previously reported structure [22] for a doubly deprotonated, isolated PA molecule adsorbed on MgO(100), which was optimized for comparison, is depicted together with the two most stable results of the optimization for the saturated monolayer (1 ML). The calculated adsorption energy per PA molecule for the isolated molecule in Fig. 5a is 2.73 eV. We also tried to calculate an isolated singly deprotonated adsorbed PA molecule. However, during the geometry optimization the singly deprotonated starting structure turned into a doubly deprotonated adsorbed PA molecule. This suggests that, at least for isolated PA molecules, a singly-deprotonated adsorption mode is not stable and deprotonation proceeds to the doubly-deprotonated single bridging bidentate compound (type Fig. 1, h). This indicates that there might be a tendency to complete deprotonation once a hydrogen-bonded trimer of intact PA molecules is broken up and deprotonation starts.

For the saturated ML with four PA molecules on a 3×4 MgO(100) surface, two stable structures, shown in Fig. 5b and c, one with singlyand one with doubly- deprotonated PA molecules, were identified, corresponding to the schematic structures h and e of Fig. 1, with adsorption energies of 2.59 and 2.25 eV, respectively. This means for the saturated ML the calculated energy of the structure with singly deprotonated PA molecules is more stable than the fully deprotonated one. This is different from the situation found for isolated PA molecules. However, in experiment, when we add molecules to the surface one by one, we will have doubly-deprotonated species in the beginning. Once a doubly-deprotonated structure is formed a re-protonation requires breaking of an oxygen-magnesium bond including rearrangements of the involved magnesium atom back into the surface from which it was pulled out to some extent, upon interacting with PA, see Fig. 5c. This suggests that re-protonation requires a considerable activation energy and thus is kinetically hindered in the considered temperature range. In experiment, therefore, the doubly-deprotonated structure should be present even if it has a somewhat higher energy. Moreover, the calculated energies of the ML may be a bit less accurate than that of an isolated PA molecule, because we had to choose a supercell of moderate size and had to make assumptions on the positions of the hydrogen atoms. The latter were placed at free surface oxygen atoms in the immediate vicinity of the adsorbed PA molecules. For a larger supercell other structures with the same coverage but different energetical ordering could emerge. Moreover, it can be assumed that the protons are highly mobile and might diffuse to defects or form other structural motives that could not be considered here. Conclusions on the actually present structure are therefore not exclusively drawn from the calculated energies but are scrutinized and confirmed by the comparison of calculated and measured XP spectra.

To that end, the core level binding energies were calculated and by placing a Gaussian function with a width of 0.3 eV on each of them XP spectra were simulated (depicted in Fig. 4). In general, only relative values can be compared, however, the energetic order of the calculated core levels should reflect the experimental findings. For this reason, the given values were calculated as centers of gravity for each peak from the average of the unbroadened core level binding energies contributing to the peak. The values are given with respect to a reference species, usually the bulk MgO core levels. Furthermore, all shifts of binding energies from the reference are smaller than in the experiments. The O 1s spectrum of the calculated trimer molecules, Fig. 4, exhibits two broad peaks (violet). The peak shifted by 1.8 eV stems from the carbonyl and the second peak shifted by 3.2 eV from the protonated oxygen atoms. In the C 1s spectrum the peak for the carboxylic carbon atoms is at 2.8 eV higher binding energy than the aromatic carbon signal. For the half-deprotonated molecules in Fig. 4b, the O 1s levels of the carboxylic oxygen atoms (violet) are found at 1.4 eV and 2.7 eV higher binding energy than the oxygen atoms of the MgO surface. Additionally, the signal of the newly formed surface hydroxyl oxygens appears with a shift of \sim 2.4 eV (orange). For the doubly deprotonated structure in Fig. 4c, a single O 1s peak is found with a shift of ~1.4 eV with a shoulder towards lower binding energy (violet). The additional peak (orange) with ~ 2.0 eV higher binding energy than the unprotonated surface oxygen results from hydroxyl groups by protonating surface oxygen atoms. This peak is not resolved in the experimental data though. The additional peaks located below 530 eV are modified substrate peaks originating from the unprotonated first surface layer atoms neighbored to protonated ones. Since the O/C ratio at 300 K is 3.3:1, that is, significantly higher than the ratio of 2.0:1 expected for carboxylic acid, it seems to be likely that surface hydroxyl species are contributing to a joint broad peak with the carboxylic oxygen in experiment. The C 1s spectra can also be reproduced well with a predicted core level shift of \sim 2.9 eV of the carboxylic carbon against the benzene signal. Concluding, the calculated core level shifts are in line with the formation of the doubly deprotonated species at 300 K.

In addition to the profound changes observed in the C 1s and O 1s



Fig. 4. Calculated photoemission spectra derived from structures of phthalic acid on the MgO surface shown in Fig. 5. Cyan corresponds to the MgO(100) bulk reference. In the O 1s region the O atoms of the second surface layer and in case of the Mg 2p region the Mg third layer are summed up. The orange curve in the O 1s region represents the signals of the topmost surface atoms, and the violet curves belongs to carboxylic oxygen atoms. For the Mg 2p orange is the combined signal for the topmost surface layer and green stems from the atoms in the second layer. For the C 1s the green curve includes the aromatic carbon and the orange curve the carboxylic carbon atoms. The gray curves are the sum spectra shifted along the y-axis to avoid overlapping.

spectra, surprisingly, the adsorption of phthalic acid also noticeably modifies the Mg 2p spectrum in Fig. 2 (right panel). The clean MgO(100) surface displays the main oxide component at 50.1 eV (blue) and a surface core level-shifted component at 50.8 eV (green). The latter stems from the surface atoms with an electron density different from that in the bulk. A Bader charge analysis [82-85] for the pristine surface yielded a slight difference of 0.01 electrons, but the calculation of the core level shifts could confirm the shift of 0.7 eV. A similar shift (+0.65 eV) was first observed for MgO(100) surface by Nelin et al. [54], who described it in terms of the difference of the Madelung potentials for the bulk and surface atoms. Adsorption of phthalic acid leads to a strong decrease of this feature. Upon heating, a new Mg 2p component rises at 51.3 eV (+1.2 eV from MgO; orange) and is visible in the range 250 -600 K (rises in Fig. 2). This additional species can be also found in the XP spectrum calculated for the doubly-deprotonated structure (Fig. 4). It occurs due to the lifting of magnesium atoms out of the surface layer. Those atoms are strongly bound to two oxygens of carboxylic acid groups of two neighboring molecules. The involvement of two molecules suggests that this species should occur only at high coverages. The observed shift of $\sim +0.8$ eV vs the bulk is comparable to the experimental findings (+1.2 eV). We suppose that this new component corresponds to half of the first-layer Mg atoms bounded to anchored phthalic acid molecules forming a densely packed structure (Fig. 4). This behavior further confirms the strong interaction between the Mg surface atoms and the carboxylic group. We conclude that phthalic acid adsorbs in doubly-deprotonated form at room temperature. This is indicated by 1) a single component in the O 1s spectra corresponding to one type of oxygen atoms in molecule; 2) an O/C ratio of \sim 3, which is higher than the expected 2 for intact molecules, but fits to the doubly deprotonated species; 3) a new component in Mg 2p photoemission spectrum with strong shift towards higher binding energies that is only expected, if Mg atoms are bounded to doubly-deprotonated species as confirmed by DFT analysis.

Now, after discussing the binding motif of phthalic acid on MgO (100) in the temperature range 110–550 K, we move further discussing its nature at higher temperatures. Subsequent annealing to 650 K leads to the desorption of either intact phthalic acid or decomposed fragments (Fig. 3) and a carbonization of the remaining molecules, as indicated by the broadening of the benzene C 1s component and the disappearance of the carboxylate C 1s and O 1s components in Fig. 2. It is worth mentioning that, in contrast to phthalic acid adsorbed on Ag (100) [43], its decomposition at the MgO(100) surface proceeds without the formation of stable intermediates such as phthalic acid anhydride. The latter should appear in the O 1s spectrum as two components at 533.2 (C-O-C) and at 531.8 eV (C=O) with a 1 : 2 ratio. [43]



a) Single PA 2.73 eV

b) Singly deprotonated PA 2.59 eV c) Doubly deprotonated PA 2.25 eV



Fig. 5. Geometries from DFT calculations: (a) single PA molecule with both carboxylic acid groups deprotonated and bound to the oxide surface; (b) 1 ML coverage of PA (4 PA molecules on a 3×4 surface cell) with each molecule bound via one deprotonated and one protonated carboxylic acid group; (c) 1 ML coverage of PA with each molecule bound via two deprotonated carboxylic acid groups; blue: magnesium, red: oxygen, black: carbon, white: molecular bound hydrogen, green: surface hydrogen.

3.1.2. Phthalic acid adsorption in the submonolayer coverage range

Next, we address the adsorption of phthalic acid in the submonolayer coverage, where we observe the formation of the carboxylate bond to the MgO(100) surface already at much lower temperatures than for deposition of 2.3 ML. Since, at a coverage of 2.3 ML the carboxylic groups at the interface are strongly attenuated, it is difficult to make accurate observations about the chemical state of the carboxylic groups at the interface. As is evident from Fig. 6 (topmost spectra), the adsorption of a 0.4 ML film at 110 K leads to the rise of pronounced carboxylate components in both the O1s and the C 1s spectra (orange peaks), which indicates that the anchoring of the phthalic acid starts directly upon deposition at this low temperature. In parallel, also intact carboxylic acid groups (violet peaks) are still observed on the surface. The conversion yield of intact acid groups to the carboxylate-bound species is 44% and 55%, as calculated from the O 1s and C 1s spectra, respectively. This 11% discrepancy is most likely caused by coadsorbed water molecules and hydroxyl groups (532.3 eV) on the MgO surface, contributing to the O 1s spectrum. This is also reflected by the very high O 1s vs C 1s carboxylic acid component area ratio of about 5:1 in Fig. 3b (blue circles). After the desorption of the water, which occurs up to 250 K [81], this ratio then changes to similar values as for the higher coverage experiment (orange squares). The adsorption of these species at low temperatures from the residual gas atmosphere is frequently observed for such surfaces [80,86]. The composition of the pristine surface calculated from Al Ka photoemission data (not shown) indeed yields a stoichiometry ${\rm MgO}_{1.1},$ which within our accuracy, is in line with the presence of hydroxyl species. The Mg atoms affected by the anchored molecules are barely visible in the Mg 2p spectrum, due to the lower coverage of carboxylate-bound molecules as compared to the 2.3 ML sample. Subsequent annealing results in a complete conversion of phthalic acid to the carboxylate-anchored species at 250 K, as is indicated by the disappearance of the C=O signals at 289.9 and 533.2 eV in Fig. 6. The observed species at 110 K could indicate a coadsorption structure of intact phthalic acid and doubly-deprotonated carboxylate, or it could indicate the presence of singly-deprotonated molecules. The

very small C 1s peak at 284.0 eV is attributed to magnesium carbide in the oxide matrix with the binding energy shifted from pure magnesium carbide as previously observed from 281.3 to 282.8 eV [87]. This carbide is possibly formed due to the reduction of the oxide surface by phthalic acid. The small peak at 286.6 eV corresponds to a small co-deposited contamination at unoccupied sites of the oxide surface. In contrast to the multilayer regime (2.3 ML), phthalic acid at submonolayer coverage shows a lower thermal stability; this is concluded from the fact that annealing up to 600 K yields an almost clean surface (compare O 1s spectra in Fig. 2 and Fig. 6). We conclude that densely-packed structures of phthalic acid multilayers are more resistant to the temperature decomposition, possibly due to additional intermolecular interactions like π - π stacking.

In Fig. 7, we take a closer look at the carboxylate formation at 110 K as a function of coverage. As mentioned above, the conversion yield of intact acid groups to the carboxylate-bound species is \sim 50% for the 0.4 ML film. Upon increasing the coverage to 0.8 ML, the fraction of intact acid groups (violet peaks in Fig. 7) increases to a larger extent than the amount of anchored, carboxylate-bound molecules (orange peaks), as deduced from the O 1s and C 1s spectra in Fig. 7. From this behavior, it must be expected that the 2.3 ML sample also contains a significant amount of carboxylate species. However, the strong attenuation of the photoemission signal (by \sim 75% per layer, at the low kinetic energy of ~100 eV in our experiments) makes this carboxylate-oxide bond feature unresolvable for the 2.3 ML sample. On the basis of temperateprogrammed IR studies, Xu et al. [22] proposed that upon increasing the coverage phthalic acid can change its binding motif in the first layer from a double bidentate to a single bidentate carboxylate both at 100 and 300 K. The authors tentatively associate an unknown band in the IR spectrum as the surface becomes more crowded with an OCO stretching mode from single bidentate carboxylate structures. We cannot confidently distinguish these two species in XPS at 100 K; however, we claim that at 300 K phthalic acid binds exclusively as double bidentate species since the region corresponding to unbound carboxylic groups shows no signals, both in C 1s and O 1s photoemission spectra in Fig. 7.



Fig. 6. O 1s (left), C 1s (center) and Mg 2p (right) XP spectra of 0.4 ML of phthalic acid deposited on MgO(100) substrate at 100 K, followed by stepwise annealing. XP spectra were measured at ultimate surface sensitivity with an electron kinetic energy of 100 eV for each core level, by using photon energies of 160 eV for the Mg 2p, 380 eV for the C 1s, and 650 eV for the O 1s regions. Dots show experimental data, while solid lines represent fitted curves.

3.2. Orientation of phthalic acid molecules anchored to MgO(100)

The adsorption of phthalic acid anchored to MgO(100) is further analyzed by investigating the unoccupied and occupied molecular levels by means of NEXAFS (Fig. 8) and valence band photoemission studies (Fig. 9). The O K-edge NEXAFS spectrum of the clean MgO(100) surface displays the dominant features between 537 and 544 eV that are usually observed for such films, [59] as was reviewed in detail by Frati et al. [88]. Due to the dominating character of these substrate signals, only minor changes are observed upon adsorption of multilayers or submonolayers of phthalic acid. We therefore concentrate on the C K-edge NEXAFS spectra.

The C K-edge spectra of multilayers (2.3 ML) of intact phthalic acid are characterized by dominant sharp C 1s $\rightarrow \pi^*$ transitions at 284.9 and 288.3 eV, which are assigned to the phenyl ring and the carboxylic acid group, respectively, based on the literature for benzoic, trimesic, terephthalic and isophthalic acids [23,44-46, 89]. The minor peak at 290.6 eV corresponds to another C 1s $\rightarrow \pi^*$ transition of the phenyl ring, and the three blurred resonances at 293.0, 296.0 and 300.1 eV to C 1s $\rightarrow \sigma^*$ transitions [46,90]. As mentioned, the O K-edge spectra show much weaker signals. Nevertheless, a small, but distinct π^* resonance associated with the carboxyl group is observed at 531.4 eV.

The C K-edge NEXAFS spectra after deposition of 0.4 ML phthalic acid on MgO(100) at 110 K and after subsequent annealing to 350 K show a similar resonance structure than the intact multilayers, in terms of the number and position of peaks. However, at this low coverage, the spectra exhibit a pronounced linear dichroism, that is, a huge difference between normal (90°) and grazing (10°) X-ray incidence. This observation indicates an inclined orientation of the anchored phthalic acid molecules as compared to the intact ones. The intensity of the π^* resonances, I_{π^*} , depends on the orientation of the electrical field vector of the incident synchrotron light relative to the transition dipole moment of



Fig. 7. O 1s (left), C 1s (center) and Mg 2p (right) photoemission spectra of 0.4, 0.8, 2.3 ML of phthalic acid deposited on MgO(100) substrate at 110 K. XP spectra were measured at ultimate surface sensitivity at an electron kinetic energy of 100 eV for each core level, by using photon energies of 160 eV for the Mg 2p, 380 eV for the C 1s, and 650 eV for the O 1s regions. Dots show experimental data, while solid lines represent fitted curves.

the phthalic acid molecules, which is oriented normal to the plane of the aromatic ring. For substrates with 3-fold or higher symmetry, the different azimuthal orientations of the molecules are averaged and the intensity depends only on the incident X-ray angle α and the polar tilt angle of the molecule δ as described by Stöhr using the following equation [91]:

 $I_{\pi^*}(\alpha, \ \delta) \propto P \cos^2 \alpha \left(1 - 3 \ / \ 2 \cdot \sin^2 \delta\right) + 1 \ / \ 2 \cdot \sin^2 \delta \tag{3}$

where *P* is the polarization factor of the synchrotron light.

After normalizing the spectra to the edge jump, we calculate the $I_{\pi^*}^{Gl}(\delta)/I_{\pi^*}^{Ml}(\delta)$ ratio for the resonance of the phenyl ring and estimate the polar tilt angle δ of the molecule using Eq. (3), with P = 0.8 for the Material Science beamline. Using only two incidence angles α does not allow for determining this angle with high accuracy, but it will give us a general trend. For the as-deposited submonolayer at 110 K, we obtain a polar tilt angle of the molecular plane relative to the substrate normal of $\delta = 24^{\circ}$, and for the submonolayer annealed at 350 K an angle of $\delta = 21^{\circ}$ This indicates a mostly upright standing adsorption geometry as expected for carboxylate-anchored species. For the higher coverage of 2.3 ML we calculate an angle $\delta = 41^{\circ}$ The higher value is consistent with a mixture of a disordered multilayer (54°) on top of an ordered monolayer.

The photoemission data also contain some indirect information of the orientation of the molecules: The intensity ratio of the C 1s signals of benzene and of the carboxylic acid groups calculated from C 1s spectrum of the as-deposited phthalic acid in Fig. 2 is 8:2. Notably, this value is higher than the ratio of 6:2 expected for the intact molecule. We attribute this observation to the high surface sensitivity achieved when measuring XP spectra with ~100 eV kinetic energy, where e.g. the topmost molecular layer attenuates ~75% of the signal from other layers underneath. The larger than expected value thus indicates a preferential orientation of the phthalic acid molecules in the outermost surface layer of the multilayer with the benzene rings pointing towards the vacuum, thereby attenuating the carboxylic group. Subsequent annealing (and desorption of the multilayers) leads to an even larger increase of the benzene/carboxylate ratio to 12:2, evidencing the anchor bond formation and the related preferential orientation of the molecule's benzene ring with a mostly upright standing geometry.

3.3. Temperature evolution of the electronic structure of 2.3 ml phthalic acid anchored to MgO(100)

The valence band structure of the pristine MgO(100) surface in Fig. 9 is characterized by a pronounced O 2 s peak at \sim 22 eV and a broad O 2p band between 4 and 9 eV, as previously described in Refs, [52,60,61,92, 93] without any noticeable features at around E_F, which are usually attributed to various defects in the oxide structure [53,61,93]. The adsorption of phthalic acid leads to the appearance of new bands in



Fig. 8. O-K (left) and C-K (right) NEXAFS spectra of 2.3 and 0.4 ML of phthalic acid deposited on MgO(100) substrate at 110 K, and after annealing to 350 K. The spectra were acquired at grazing (10°) (blue) and normal (90°) (orange) incidence angle; the inset illustrates the experiment geometry.

Fig. 9, which we assign to the superposition of different molecular orbitals, on the basis of the gas-phase UPS data for benzoic acid (benzene with one carboxylic acid group) and trimesic acid (benzene with three carboxylic acid groups) [94]. As expected, the bands of the adsorbed phthalic acid are much wider as compared to gas-phase measurements of trimesic acid from Ref.⁹⁰ displayed at the bottom of the Fig. 9, due to the interaction with the substrate. Subsequent annealing leads to a redistribution of the bands starting at 250 K and ending at 450 K, with no new noticeable bands being formed. This observation can be explained by structural adaptation e.g. rotating of the phthalic acid molecules upon binding to the oxide surface.

4. Conclusions

By a combination of spectroscopic techniques and density-functional theory, we have shown how reactivity and binding of phthalic acid to MgO(100) surfaces change with temperature and coverage. The adsorption of phthalic acid results in a formation of mostly upright-standing carboxylate-bonded molecules even at low temperatures such as 110 K, which coexist with intact phthalic acid. The fraction of carboxylate-bonded molecules decreases with increasing total coverage.



Fig. 9. Valence band spectra of 2.3 ML of phthalic acid deposited on MgO(100) substrate followed by stepwise annealing. The excitation energy was 100 eV. Colored panels represent the bands identified according to the spectrum of gas-phase UPS of trimesic acid shown at the bottom and reproduced from [94].

Full conversion of phthalic acid to a double-bidentate carboxylateanchored species finishes at 250 K, leaving a film that is stable up to 500 – 600 K, depending on the coverage. Further annealing leads to the decomposition of phthalic acid to graphitic carbon without formation of intermediates such as phthalic acid anhydride. We expect that the results of this work will contribute to improve the understanding of binding motifs of more complex organic molecules with multiple carboxylic acid anchoring groups.

Declaration of Competing Interest

There are no conflicts to declare.

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Supplementary materials

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