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Water dissociation on MnO(1 × 1)/Ag(100)

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In this work we utilize experimental and simulation techniques to examine the molecular level interaction of water with a MnO(1 × 1) thin film deposited onto Ag(100). The formation of MnO(1 × 1)/Ag(100) was characterized by low energy electron diffraction and scanning tunneling microscopy. Density functional theory (DFT) shows MnO(1 × 1) is thermodynamically more stable than MnO(2 × 1) by ~0.4 eV per MnO. Upon exposure to 2.5 Torr water vapor at room temperature, X-ray photoemission spectroscopy results show extensive surface hydroxylation attributed to reactivity at MnO(1 × 1) terrace sites. DFT calculations of a water monomer on MnO(1 × 1)/Ag(100) show the dissociated form is energetically more favorable than molecular adsorption, with a hydroxylation activation barrier 0.4 eV per H₂O. These results are discussed and contrasted with previous studies of MgO/Ag(100) which show a stark difference in behavior for water dissociation.

1. Introduction

Understanding the surface chemistry of manganese oxides has important implications in catalytic,^{1–4} electrochemical,^{5,6} magnetic,^{7–9} and atmospheric aerosol^{10–12} processes. Manganese oxide films have been employed in a number of applications, including ion exchange,¹³ sensors,¹⁴ electrodes^{15,16} and catalytic materials.¹⁷ In order to elucidate fundamental chemical, structural and electronic information, molecular level investigations of metal oxide films are needed.^{18,19} Fundamental studies of MnO thin films have been performed on a number of supports, including Rh(100),²⁰ Rh(111),²¹ Pt(111)^{22–25} and Pd(100).^{26,27} MnO on Ag(100) has been fairly well characterized utilizing a number of surface techniques, including low energy electron diffraction (LEED),^{28–33} X-ray photoelectron diffraction (XPD),^{30,31} near edge X-ray absorption fine structure (NEXAFS)³² and X-ray photoelectron spectroscopy (XPS).^{29,32,34} MnO films on Ag(100) are tetragonally distorted due to the lattice mismatch of about 9%.³⁵ MnO thin films show distortion for the first few nm, while thicker films greater than 5 nm adopt a bulk MnO structure and lattice constants.³¹

Rumpling of the top layer of a cleaved MnO(100) single crystal shows an outward displacement of Mn,³⁶ while multilayer MnO/Ag(100) shows significant rumpling of the oxygen atoms towards the vacuum.²⁸ This difference may be explained by the strain films have imparted from the Ag(100) substrate mismatch. To our knowledge there is currently only one scanning tunneling microscopy (STM) study of MnO films on Ag(100), observing MnO(2 × 1) nanostripes which first-principle analyses showed to be a metastable state compared to (1 × 1).³³ Additional STM and molecular simulation studies are needed to characterize the thermodynamically stable MnO(1 × 1) on Ag(100).

Water adsorption and hydroxylation at metal oxide surfaces are known to affect interfacial electronic properties and surface reactivity.^{37–42} The reduction of NO on manganese oxides is affected by the presence of water.⁴³ The degree to which hydroxylation occurs over metal oxides depends upon the surface chemistry and morphology. In order to assess the potential impact surface hydroxylation has on heterogeneous reactions, careful studies are needed to quantitatively assess the extent of hydroxylation. We performed a joint theoretical and experimental investigation to examine the interaction of water with submonolayer MnO(1 × 1) deposited onto Ag(100). Film quality was assessed using LEED and STM, and surface hydroxylation was identified using XPS before and after exposure to water vapor. To our knowledge there are currently no molecular simulations examining water dissociation on MnO. Herein we examine MnO film properties on Ag(100), the adsorption of water and the tendency of water to dissociate at the film surface using hybrid functionals using DFT and adopting a periodic approach.

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2. Methods

2.1. Experimental details

Experiments were performed at the Center for Functional Nanomaterials at Brookhaven National Laboratory using an ultra-high vacuum (UHV) system consisting of three chambers, including an analysis chamber, preparation chamber, and a fast entry chamber. X-ray photoelectron spectroscopy (XPS) spectra were collected in the preparation chamber with base pressures $< 2 \times 10^{-9}$ Torr using a hemispherical electron energy analyzer (SPECS, PHOIBOS 100) and twin anode X-ray source (SPECS, XR50). Al K_{α} (1486.6 eV) radiation was used at 10 kV and 30 mA. The angle between the analyzer and X-ray source is 45° and photoelectrons were collected along the sample surface normal. Ag 3d, C 1s, Mn 2p and O 1s spectra were collected using 20 eV pass energy. Binding energies were referenced to Ag 3d(5/2) at 368.3 eV.⁴⁴ XPS peaks were analyzed using peak fitting software (Casa Software Ltd) with a Shirley background subtraction and 80/20 Gaussian–Lorentzian fits. Scanning tunneling microscopy (STM) was performed in the analysis chamber (RHK 700, VT-STM/AFM) at room temperature with images captured under pressures of $< 3 \times 10^{-10}$ Torr. The Ag(100) crystal was mounted onto the sample holder (see ESI,[†] Fig. S1). During XPS measurements the crystal was grounded through a thermocouple attached on the crystal back side, while during STM the sample bias was applied between the sample and grounded STM tip. STM images were acquired under constant current mode with home-built electronics and GXSM software. Tungsten STM tips were electrochemically etched in a 0.10 M KOH solution and sputtered *in vacuo*. STM images were processed using ImageJ software.⁴⁵

The Ag(100) single crystal (Mateck, 99.999%, $< 0.4^{\circ}$ polishing) was cleaned by multiple cycles of sputtering in 10^{-5} Torr Ar at 1.5 kV and subsequently annealed to 700 K. Low energy electron diffraction (LEED) images showed good sample quality with sharp (1×1) diffraction spots (ESI,[†] Fig. S2a). STM of the Ag(100) showed consistent large flat terraces (ESI,[†] Fig. S3). MnO thin films were prepared by e-beam evaporation (Mantis Deposition LTD, QUAD-EV-C Mini) at a rate of ~ 1 ML min^{-1} monitored using a quartz crystal microbalance (Inficon, Qpod). The MnO films were deposited from a Mn rod (Goodfellow, 99.99%) in 10^{-7} Torr O_2 with the Ag(100) substrate held at room temperature, followed by annealing in vacuum to 800 K.²⁹ Water vapor exposures were performed in the fast entry chamber which was baked and maintained a base pressure of $< 2 \times 10^{-8}$ Torr. The fast entry chamber was equipped with a precision leak valve, behind which was a custom glass bulb containing 18.2 M Ω cm water (Aqua Solutions, 2122A) which was freeze-degassed at least three times prior to the start of experiments. After exposure to water, the fast entry chamber was pumped down and the sample was transferred for XPS analysis under UHV.

2.2. Simulation details

DFT calculations were performed with a periodic approach, using a localized Gaussian type functions (GTF) basis set

implemented in the CRYSTAL09 code.⁴⁶ For surface calculations, CRYSTAL adopts periodic slab models characterized by two infinite dimensions (x and y) and a finite thickness. An Ag slab, at the experimental lattice parameter, has been used to model the metal substrate. We have verified that the use of the optimized lattice parameters for Ag does not change the results. The MnO overlayer is adsorbed on both sides of a 5-layer slab. This model has been shown to provide a satisfactory description of the metal substrate in many cases of metal–oxide interactions.^{47–51} The properties of MnO monolayer on Ag(100) were modeled with (1×1) and (2×1) unit cells for the square and distorted hexagonal structure, respectively, and both ferromagnetic (FM) and antiferromagnetic (AFM) magnetic configurations have been considered. For the (1×1) , the AFM solution was obtained using a (2×1) unit cell with opposite spin on the two Mn^{2+} ions.

Adsorption of an isolated water molecule was modeled using a $(2\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ supercell (8 Mn and 8 O) with respect to the Ag(100) surface and corresponds to a coverage $\Theta = 1/8$ ML. All coordinates of the adsorbates, oxide films and the Ag substrate were allowed to relax. Two different GTF basis sets have been employed: basis set A of triple zeta quality used for geometry relaxations and a larger one, B, of quadruple zeta quality for the valence, has been employed for accurate estimates of energetics. Basis A consists of all-electron $[311-1]/(3s1p)$ and $[511111-411-1]/(6s3p1d)$ functions for H and O, respectively, Hay–Wadt relativistic small core pseudopotentials⁵² (15 electrons) together with $[31111-311]/(5sp3d)$ contracted GTF functions for Mn and Hay–Wadt relativistic small core pseudopotentials⁵² (19 electrons) together with $[2111-31]/(4sp2d)$ contracted GTF functions for Ag. Basis B consists of all electron $[6211111-4111-11-1]/(7s4p2d1f)$, $[3111-11-1]/(4s2p1d)$ for O and H,⁵³ $[84111111-621111-3111-1]/(10s6p4d1f)$ GTFs for Mn⁵⁴ and Stuttgart relativistic small core pseudopotentials⁵⁵ (15 electrons) together with $[3111-2111-2111]/(5s4p4d)$ contracted GTF functions for Ag. With basis A the basis set superposition error (BSSE) has been checked to be less than 0.15 eV but with basis B it does not exceed 0.05 eV.

In CRYSTAL calculations the level of accuracy in evaluating the Coulomb and the exchange series is controlled by five parameters⁵⁶ for which 10^{-7} , 10^{-7} , 10^{-7} , 10^{-8} , 10^{-16} values have been used for all calculations. The convergence threshold for SCF energy was set to 10^{-8} Ha. The reciprocal space was sampled according to a regular sub-lattice determined by the shrinking factor⁵⁶ which was set to 12 (50 independent k -points in the irreducible part of the Brillouin zone) for the $(2\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ supercell. A Fermi–Dirac smearing procedure has been adopted with the smearing parameter of 0.01 a.u. Geometry optimizations have been carried out using analytical gradients with respect to atomic coordinates and convergence threshold for atomic forces was set to $0.005 \text{ eV } \text{\AA}^{-1}$. BSSE has been evaluated by applying the standard counterpoise method.⁵⁷ The hybrid PBE0⁵⁸ functional has been used for all calculations since it has been reported to provide a feasible description of the adsorption properties of surface adsorbates.^{59–61} In addition test calculations have also been

performed with B3PW,^{56,62} found to be particularly suitable for the study of magnetic metal/oxide heterostructures,⁴⁷ and the range separated HSE06.^{63,64}

The properties of MnO film on Ag(100) were also computed with a fully periodic approach and a plane waves basis set, as implemented in the VASP code.^{65,66} For these calculations the electrons-ions interaction was described within the projector-augmented plane-wave (PAW) method,⁶⁷ employing a 400 eV energy cutoff. Six valence electrons were explicitly treated for oxygen ($2s^2 2p^4$), 13 for manganese ($3p^6, 3d^5, 4s^2$) and 11 for silver ($4d^{10} 5s^1$). A $(4 \times 4 \times 1)$ Monkhorst-Pack k -points mesh is used for the $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ supercell. Methfessel-Paxton and Gaussian smearing procedures have been used for conducting and insulating systems, respectively (smearing parameter = 0.1 eV). Calculations were performed at both PBE level,⁶⁸ to compare the results obtained with CRYSTAL code with the same functional, and with DFT+ U ^{69,70} (PBE+ U functional), more suitable for transition metal oxides. U_{eff} for Mn d states has been set to 4 eV, as determined by fitting the formation enthalpies of oxides.^{71,72} The MnO overlayer is adsorbed on one side of a 4-layer Ag slab. The slabs were separated by at least 13 Å of vacuum and the dipole correction is applied in order to eliminate the residual dipoles in the direction perpendicular to the surface. All the coordinates except the two bottom Ag layers were allowed to relax and the convergence threshold for atomic forces was set to 0.01 eV Å⁻¹. As described below, the strain energy for the (1×1) over-layer is greater at the DFT+ U level compared to the other functionals. The enhanced strain produces a reconstruction of the film in the $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ supercell where the film is strongly rumpled, indicating that the current implementation of DFT+ U is not well suited for this system. A similar problem has been reported for the MnO₂ molecule⁷³ where DFT+ U was found to overestimate the Mn-O bond length. In that work a new method, DFT+ U + V (at the moment not implemented in standard codes), has been proposed, which provides a better description of bond angles and as a result of bond lengths. Due to this limitation of DFT+ U for this specific system for our water adsorption study we only used hybrid functionals, as implemented in CRYSTAL.

3. Results

3.1. STM and XPS

Results of a freshly prepared MnO/Ag(100) film are shown in Fig. 1a. Most of the silver substrate is covered with an extended single layer of MnO with intermittent square islands forming on top. The cubic nature of the images is indicative of a (1×1) MnO structure on Ag(100), further evidenced by LEED results (ESI,† Fig. S2b). Three representative line scans are shown in Fig. 1b. Trace 2 (black) tracks a line profile from the edge of one extended monolayer film to another, with the Ag(100) substrate in between. The apparent height in this first layer is ~ 0.2 nm. Trace 1 (red) shows the profile of an island on top of the extended MnO monolayer film. The apparent height of this

island is similar to that of the extended MnO monolayer film (trace 2). This suggests the isolated islands are a second layer of MnO on top of the extended underlying MnO. Dark STM features roughly 5 nm across are also seen in the interior of the extended MnO monolayer film with apparent heights of ~ 0.08 nm (trace 3). Given the lack of atomic resolution for this instrument, it is difficult to assess the nature of these dark spots although they may be due to voids in the extended MnO film. Such dark features were not observed previously for a (2×1) MnO/Ag(100) film.³³ Based on the image in Fig. 1a we estimate the MnO coverage to be 0.9 ML.

Results of Mn 2p(3/2) and O 1s XPS spectra are shown in Fig. 2. The initial Ag(100) substrate is devoid of Mn and O species (Fig. 2(i)). Upon deposition of a freshly prepared MnO film, the Mn 2p(3/2) spectrum in Fig. 2a(i) shows a peak at 641.1 eV binding energy (BE) consistent with Mn²⁺ for both bulk MnO and supported MnO films.^{26,29,74,75} These results confirm the complete conversion of Mn⁰ (BE = 639 eV) to MnO during deposition where the O₂ pressure was held at 10⁻⁷ Torr to maintain an Mn²⁺ oxidation state without further converting the film to higher Mn oxidation states. The O 1s spectrum of

Fig. 1 STM results of a freshly prepared MnO film annealed in vacuum to 800 K. (a) 200 × 200 nm image collected at -2.0 V and 0.40 nA. (b) Apparent height profiles.

Fig. 2 (a) Mn 2p(3/2) and (b) O 1s XPS spectra taken of (i) silver substrate, (ii) as deposited film of MnO, (iii) MnO film after 5 minute exposure to 9.0×10^{-3} Torr H_2O and (iv) after exposure to 2.5 Torr H_2O .

the freshly prepared film (Fig. 2b(ii)) shows a main feature at a BE of 529.9 eV due to the oxide (Ox) peak of MnO, and a smaller peak at a higher BE of 531.6 eV attributed to hydroxyl (OH) groups. The BE difference of 1.7 eV is consistent with the spacing between Ox and OH for the surface of a MnO single crystal.⁷⁶ We attribute this initial hydroxyl feature to the dissociation of residual gas phase water background at low coordinated defect sites (*i.e.*, kinks, edges, corners) on the freshly prepared MnO film. The potential contribution of OH species from oxidized adventitious carbon was found to be negligible based on C 1s spectra composed primarily of C-H species at 285.0 eV (ESI,† Fig. S4).

Upon exposing the freshly prepared MnO film to a water vapor pressure of 9×10^{-3} Torr for 5 minutes at room temperature, the Mn 2p(3/2) remains similar to the freshly prepared film (Fig. 2a(iii)) while the O 1s high binding energy OH feature increases relative to the Ox peak (Fig. 2b(iii)). These results indicate that the oxidation state of Mn remains the same (Mn^{2+}) while there was an increase in water dissociation forming hydroxyl groups. The decrease in bulk oxide signal at 529.9 eV is attributed to the conversion of surface Ox species to surface OH; a similar conversion was reported for MgO/Ag(100)

Fig. 3 Ratio of OH peak area to total O 1s peak area for the initial (as deposited) MnO film, after exposure to 9.0×10^{-3} Torr H_2O , then 2.5 Torr H_2O . Water exposures were 5 min.

films exposed to water vapor.^{77,78} Water vapor exposures to an MnO(100) single crystal showed that above a pressure “threshold” of 10^{-4} Torr at room temperature the MnO surface significantly hydroxylates.⁷⁶ Thus, our results of increased hydroxylation at an exposure of 9×10^{-3} Torr at room temperature are consistent with these observations. The MnO film was additionally exposed to 2.5 Torr for five minutes. The Mn 2p(3/2) peak (Fig. 2a(iv)) remained similar to the first water exposure. The Ox peak decreased while the OH peak increased in the O 1s spectrum (Fig. 2b(iv)) relative to the 9×10^{-3} Torr exposure. Fig. 3 plots the OH peak area relative to the total O 1s peak area for the freshly deposited MnO film, 9×10^{-3} Torr exposure and 2.5 Torr exposure. These results show that the surface OH species increases from 33% under vacuum conditions to 66% after exposure to 2.5 Torr (12% relative humidity).

3.2. Simulations

3.2.1. The MnO monolayer on Ag(100). The square MnO(1 $\times$ 1) overlayer is derived from a monolayer cut along the 100 direction of MnO bulk. The (100) isolated oxide monolayer exhibits a considerable contraction with respect to the bulk structure: the 2D lattice constant (a) using the PBE0 functional at equilibrium is reduced to 2.963 Å ($a = 3.147$ Å is the corresponding computed value for the bulk, in good agreement with XRD data^{79,80}) resulting in a practically perfect matching with Ag ($a = 2.892$ Å)⁸¹ and a vanishing energy strain ($\Delta E_s = 0.02$ eV per MnO, see Table S1, ESI†). Interestingly, the strain energy is method-dependent (Table S1, ESI†). In particular, it is considerably more pronounced at DFT+ U level where the optimized lattice parameter is closer to the bulk value and the unsupported film is more rigid due to DFT+ U difficulties in describing bond angles.⁷³ Similar contractions of monolayers as found at PBE0 level have been reported for NiO and MgO.^{49,82,83} Once supported on the Ag(100) surface, MnO achieves a perfect epitaxy match with the substrate where the equilibrium configuration corresponds to oxygen ions on top of the surface Ag atoms ($d_{\text{Ag-O}} = 2.598$ Å, PBE0/A-basis) as shown

Fig. 4 Side and top views of (a) (1×1) and (b) (2×1) MnO monolayers supported at the Ag(100) surface. The blue, red and light grey circles identify Mg, O and Ag atoms, respectively.

in Fig. 4a. The adsorbed film is slightly corrugated with Mn closer to the surface by $0.1 \text{ \AA}$ with respect to O. The adhesion energy (ΔE_{ad}) is about -0.30 eV per MnO, irrespective of the adopted Hamiltonian (Table S1, ESI[†]). Comparable values of ΔE_{ad} have also been reported for Pd- and Ag-supported MgO and NiO monolayer, with values between -0.3 and -0.4 eV per MO ($M = \text{Mg, Ni}$).^{82–85} The relatively weak interaction with the substrate does not affect significantly the electronic and magnetic properties of the supported MnO film. The antiferromagnetic (AF) order is always favored over the ferromagnetic (FM) one by several tenths of eV per MnO in both the unsupported and supported MnO film (Table S2, ESI[†]). However, a weak polarization of the composite system, resulting in a slightly positive charge of the overlayer, can be inferred by a Mulliken population analysis, which shows a small accumulation of negative charge on Ag atoms, $\Delta q(\text{Ag}) \approx 0.14e$ per surface Ag (PBE0/A-basis) and a depletion on the MnO oxygen ions.

The distorted hexagonal (2×1) MnO monolayer, also observed on Ag(100),³³ derives from a bilayer (a Mn and an O layer) cut along the (111) crystallographic plane of MnO bulk. Once relaxed, the unsupported film adopts a hexagonal flat structure slightly less stable (0.02 eV per MnO, PBE0/A-basis) than the corresponding (100) monolayer. The smallest coincidence cell to match the Ag substrate is a (2×1) which requires a large contraction of the MnO 2D cell, with a large energy penalty ($\Delta E_s = 0.44$ to 0.47 eV per MnO; Table S1, ESI[†]). The equilibrium configuration of the supported film corresponds to one oxygen almost on top of a surface Ag atom ($d_{\text{Ag-O}} = 2.401 \text{ \AA}$, PBE0/A-basis) and one oxygen in a bridge position ($d_{\text{Ag-O}} = 3.403 \text{ \AA}$, PBE0/A-basis) as shown in Fig. 4b. The adhesion energy ΔE_{ad} is about -0.42 to -0.45 eV per MnO, depending on the adopted Hamiltonian (Table S1, ESI[†]). Irrespective of the selected computational approach, the gain in energy upon the interface formation is comparable to the cost to squeeze the oxide to fit the metal substrate: the (2×1) MnO overlayer appears therefore to be a metastable phase and is less stable than the (1×1) by about 0.3 to 0.4 eV per MnO (Table S1, ESI[†]). As far as the magnetic properties, similarly to the (1×1) MnO film, also for the (2×1) phase the AF order is favored over

Fig. 5 Schematic view of water molecule (a) non-dissociated (ND) and (b) dissociated (D) on (1×1) MnO/Ag(100). The blue, red, dark and light grey circles identify Mg, O, H and Ag atoms, respectively.

the FM in the unsupported and supported MnO film. However, the energy differences are larger in this case, being of the order of tenths of eV (Table S2, ESI[†]).

3.2.2. Water adsorption and dissociation. Water adsorption was investigated for the (1×1) MnO phase in the most stable AF magnetic configuration. We have considered first the adsorption of isolated water molecules ($1/8 \text{ ML}$ coverage) in the molecular state. The O atom of the non-dissociated water molecule (O_w) is bound to a Mn ion ($d_{O_w-\text{Mn}} = 2.269 \text{ \AA}$, PBE0/A-basis). As seen in Fig. 5a the molecule forms a hydrogen bond with the surface, which leads to unequal intramolecular OH bonds: the OH group that interacts with the surface has a internuclear distance $d_{O_w-H_1} = 1.005 \text{ \AA}$ with a short contact with the adjacent surface oxygen ($d_{O_s-H_1} = 1.653 \text{ \AA}$, PBE0/A-basis), while the other OH distance equals $0.959 \text{ \AA}$ (PBE0/A-basis results). The adsorption energy of this non-dissociated state (ND) is of the order of -0.82 eV at the PBE0/A-basis level and does not change significantly when changing basis set and DFT functional. In particular, $E_{\text{ads}}^{\text{W}}(\text{ND}) = -0.89, -0.86$ and -0.92 eV per H_2O for PBE0, B3PW and HSE06 (larger B-basis) calculations, respectively (see Table 1 for details). $E_{\text{ads}}^{\text{W}}(\text{ND})$ is considerably larger than computed in the case of an Ag-supported MgO monolayer ($E_{\text{ads}}^{\text{W}}(\text{ND}) = -0.54$, PBE0) but close to what computed on transition metal oxides.^{86,87} The dissociated form is obtained by heterolytic splitting of the molecule with the proton bound to a surface O, $d_{O_s-H_1} = 0.944 \text{ \AA}$, and the OH^- bridging two adjacent Mn ions, $d_{O_w-\text{Mn}} = 2.084, 2.082 \text{ \AA}$, and $d_{O_w-H_2} = 1.085 \text{ \AA}$ (PBE0/A-basis results) shown in Table 1. Water dissociation causes a strong corrugation of the oxide layer, which is not hindered by the interaction with the metal support. The protonated surface oxygen (O_s) strongly relaxes outwards by $1.1 \text{ \AA}$ (PBE0/A-basis results) with respect to its position prior to water adsorption. The same happens to the Mn ions in contact with the adsorbed OH group, also lifted on average by $0.8 \text{ \AA}$ (PBE0/A-basis). The resulting MnO rumpling is $1.2 \text{ \AA}$ as compared to the rumpling of about $0.8 \text{ \AA}$ for the molecular

Table 1 Computed properties of molecular (ND) and dissociated (D) water monomer on the MnO(1×1)/Ag(100) supported monolayer. The water coverage is 1/8 ML in all cases. Structural data refer to calculations performed at PBE0/A-basis level. Distances in Å, energies in eV. See Fig. 5 for labelling of atoms

	W/MnO(1×1)	
	ND	D
$d(\text{O}_w\text{-H}_1)$	1.005	3.629
$d(\text{O}_w\text{-H}_2)$	0.959	0.956
$d(\text{O}_s\text{-H}_1)$	1.653	0.963
$d(\text{O}_w\text{-Mn}_1)$	2.269	2.081
$d(\text{O}_w\text{-Mn}_2)$	4.690	2.095
MnO rumpling	0.91	1.21
$\Delta E_{\text{ads}}^W(\text{PBE0/A})^a$	-0.82	-0.99
$\Delta E_{\text{ads}}^W(\text{PBE0/B//PBE0/A})^a$	-0.89	-0.94
$\Delta E_{\text{ads}}^W(\text{HSE06/B//PBE0/A})^a$	-0.92	-0.97
$\Delta E_{\text{ads}}^W(\text{B3PW91/B//PBE0/A})^a$	-0.86	-0.90

^a E_{ads}^W computed with respect to a free water molecule: $E(\text{W/MnO}(1 \times 1)/\text{Ag}) - E(\text{MnO}(1 \times 1)/\text{Ag}) - E(\text{W})$.

adsorption and a rumpling of about 0.3 Å for the supported oxide monolayer prior to water adsorption. The structural relaxation, already observed for the dissociated water dimers on MgO/Ag(001) films⁵⁰ can be seen as an electrostatic response to the charged nature of the dissociation fragments, as reported for spontaneously charged adsorbates on ultra-thin oxide films,⁸⁸ and contributes to the stabilization of the heterolytic dissociated state. The adsorption of the charged fragment does not change the electronic and magnetic states of MnO: the small variation of charge and magnetic moment of the two Mn ions interacting with the OH fragment ($\Delta q = 0.14$, $\Delta \mu = 0.11e$) indicates that Mn retains its oxidation state. A small but non-negligible variation of charge is also observed in the surface O bound to the proton ($\Delta q = 0.11e$) and in the Ag atoms at the interface ($\Delta q = 0.05e$).

Water dissociation at MnO(1×1)/Ag(100) is an exothermic process as shown by $E_{\text{ads}}^W(D)$ values reported in Table 1. Irrespective of the hybrid functional selected for the calculations, dissociated water on MnO(1×1)/Ag(100) is always preferred over the molecular form by about 0.16 (basis A) and about 0.05 eV (basis B). The dissociation of a water monomer on terrace sites of MgO(1ML)/Ag(100) has also been found to be thermodynamically favorable, but to a lesser extent with $E_{\text{ads}}^W(D)$ ranging from -0.16 to -0.23 eV per H₂O.^{50,89} Moreover, while water prefers to be in the dissociated state on MnO(1×1)/Ag(100) (Table 1), the molecular state of water is thermodynamically more favourable on MgO(1 ML)/Ag(100) ($E_{\text{ads}}^W(\text{ND}) = -0.50$ to -0.63 eV per H₂O^{50,89}). The significantly different behaviour of Ag-supported MnO and MgO monolayers on the stabilization of the dissociated water monomer can be ascribed to different factors. More flexible bonds in MnO (at 298 K the bulk modulus of MnO and MgO is 148.6 and 164.4 GPa, respectively^{90,91}) could favor polaronic distortion in the MnO monolayer, which is able to stabilize the charged fragments. However, the difference between the MnO and MgO bulk modulus is not enough to explain the different behaviour of the two oxides. Analysis of the Density of States (not shown)

reveals that in the case of MnO a stronger covalent bond is formed with water in the molecular adsorption and hydroxyl in the dissociated state, indicating a stronger acidity of Mn²⁺ with respect to Mg²⁺, as generally reported for transition metal oxides.⁹² The M-O_w bond involves Mn d orbitals and O_w 2p states, although a spd hybridization is also observed for the Mn states.

We now consider the kinetics of water dissociation and assess the evolution of two internal coordinates as shown in Fig. 6: $R1 = d_{\text{O}_w\text{-H}_1}$ and $R2 = d_{\text{O}_w\text{-Mn}_2}$. $R1$ describes the water deprotonation and the formation of the surface ionic couple (lines a and b), whereas $R2$ is related to the surface rearrangements that lead from a one-fold coordination of O_w in the reactant to a two-fold bridged coordination in the dissociated water (line c). Line a describes how the energy depends on variations of the $R1$ coordinate starting from the adsorbed molecule (one-fold O_w coordination), whereas line b is built from the bridged configuration of the final product. Following line a, at $R1 = 1.3$ Å, we find a small barrier ($\Delta E = 0.15$ eV per H₂O) that leads to deprotonated water; in the range of $R1 = 1.4$ to 2 Å water evolves to form a metastable surface ionic couple that can easily recombine to molecular water. At $R1 \approx 2.2$ Å the configuration with bridged O_w (line b) becomes favored. $R1$ alone is not able to describe this change of configuration. Therefore fixing $R1 = 2.2$ Å, we build the energy path associated with $R2$, line c (Fig. 6b). Following line c, we find that the change to the bridged configuration occurs approximately at $R2 = 2.9$ Å with an energy cost of about 0.15 eV per H₂O. Combining the energy profile of lines a and c we can estimate a barrier for water dissociation close to 0.4 eV. This estimate represents an upper limit of the dissociation barrier and demonstrates that the water dissociation involves a collective process, where water deprotonation is coupled with the polaronic distortion essential to stabilize the charged water fragments. While the estimated barrier is sizable, it is significantly smaller than for the Ag-supported MgO monolayer (0.56 eV per H₂O).⁸⁹ Moreover, while the process is exothermic in going from the molecular to dissociated state for MnO(1×1)/Ag(100), it is endothermic for MgO(1 ML)/Ag(100).

4. Discussion

We have prepared MnO(1×1)/Ag(100) with a nominal thickness of ~ 1 ML evidenced both by STM and LEED. Our observed MnO(1×1) structure is in contrast to Obermüller *et al.*³³ who observed a metastable (2×1) phase. This difference in phase appears to be due to differences in annealing procedures. Our films were prepared by depositing Mn in an O₂ environment at room temperature followed by annealing under vacuum to 800 K. However, films produced by Obermüller *et al.*³³ were annealed in 7×10^{-8} to 4×10^{-6} Torr O₂ at 700 to 800 K. Annealing under O₂ may be responsible for the kinetically driven transition to the metastable (2×1) phase.

The freshly prepared MnO(1×1)/Ag(100) film was observed to be partially hydroxylated under vacuum conditions

Fig. 6 Reaction path for water dissociation. The suggested reaction coordinate is a combination of $R1 = d(O_w-H_1)$ that drives the breaking of OH in water (upper panel), and $R2 = d(O_w-Mn_2)$ that drives the polaronic distortion of the MnO film to accommodate the charged fragments (lower panel). See Fig. 5 for labeling of atoms.

(Fig. 2b(ii)). We attribute this to the reactivity of residual water vapor in the chamber with MnO film nonstoichiometric defect sites (steps, kinks, corners, and sites with missing Mn and O). This is consistent with the interpretation of Brown and coworkers⁷⁶ who exposed a freshly prepared MnO(100) single crystal surface to varying water vapor pressures. Below 10^{-4} Torr hydroxylation was slow, but was observed to increase over a period of an hour. Exposures to MnO above a “threshold” pressure of 10^{-4} Torr lead to extensive and rapid hydroxylation of the surface. A similar “threshold” pressure was observed by Brown and coworkers for water vapor exposures to a MgO(100) single crystal,⁹³ and attributed the similar reactivity of MnO(100) and MgO(100) above this threshold to extensive dissociation of water at stoichiometric terrace sites on both surfaces.

In their extensive discussion comparing water reactivity with MnO(100) and MgO(100), Brown and coworkers identified a stark contrast between the two substrates below the “threshold” pressure. At low water vapor pressures MnO(100) hydroxylation was observed to increase as a function of time, while MgO(100) did not. Brown and coworkers remarked that the “reason for this difference is unclear at present and requires further investigation”.⁷⁶ Herein we wish to address this difference in reactivity.

It has been shown experimentally that extensive hydroxylation of MgO(100)/Ag(100) films occurs under ambient water vapor conditions above a threshold relative humidity of 0.01% using ambient pressure XPS.^{77,78} These results were consistent

with the vacuum studies of Brown and coworkers for single crystal MgO(100).⁹³ It was suggested by Newberg *et al.*⁷⁷ that the onset to hydroxylation was likely due to an autocatalytic dissociation process whereby water aggregation at stoichiometric terrace sites occurs, transitioning from water monomers on the surface to water dimers or trimers. Shortly thereafter Giordano and Ferrari⁵⁰ showed that while water monomers are unreactive at MgO(100) terrace sites, upon forming a water dimer one of the two waters within the dimer goes through barrierless dissociation. Thus, upon forming a water dimer at MgO terrace sites, one of the waters is dissociated into two hydroxyl groups while the other remains molecular, stabilizing the hydroxyl groups. This behavior was found to occur for monolayer MgO(100)/Ag(100) and bulk MgO(100). Proton transfer was also found to be facile, consistent with previous simulations.⁹⁴

The situation is different for water monomers on MnO(100). As seen from Table 1 for MnO(1 × 1)/Ag(100) it is energetically favorable to have a water monomer in both the molecular and dissociated state relative to gas phase water ($E_{ads}^W < 0$), where the dissociated state is more stable. Moreover, there is an energy barrier of ~ 0.4 eV in transitioning from the molecular to dissociated state. Although not calculated in the study herein, if such an energy barrier also exists for the dissociation of water on terrace sites at the interface of bulk MnO(100), this could explain the time dependent reactivity of bulk MnO(100) observed by Brown and coworkers⁷⁶ under low water vapor conditions ($< 10^{-4}$ Torr).

5. Conclusions

We have examined for the first time the hydroxylation of $\text{MnO}(1 \times 1)/\text{Ag}(100)$ by combining experiments with molecular simulations. The formation of $\text{MnO}(1 \times 1)$ on $\text{Ag}(100)$ was prepared by evaporation of Mn onto $\text{Ag}(100)$ at room temperature in the presence of 10^{-7} Torr O_2 , followed by annealing in vacuum to 800 K. Annealing in the presence of O_2 has been shown previously to form the metastable $\text{MnO}(2 \times 1)$ phase.³³ Upon exposure to water vapor, extensive hydroxylation of $\text{MnO}(1 \times 1)/\text{Ag}(100)$ occurs, consistent with previous results for an $\text{MnO}(100)$ single crystal. Molecular simulations reveal that it is energetically favorable to go from the molecular to dissociated state for a water monomer on $\text{MnO}(1 \times 1)/\text{Ag}(100)$ terrace sites with an energy barrier of ~ 0.4 eV. We believe the observations of an energy barrier for the dissociation of a water monomer on $\text{MnO}(1 \times 1)/\text{Ag}(100)$ helps elucidate previously unresolved observations⁷⁶ of time dependent hydroxylation kinetics for the dissociation of water on $\text{MnO}(100)$.

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