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Water on Oxide Surfaces: A Triaqua Surface Coordination Complex on Co\textsubscript{3}O\textsubscript{4}(111)

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Supporting Information Placeholder

ABSTRACT: The interaction of water with metal oxides controls their activity and stability in heterogeneous catalysis and electrocatalysis. In this work, we combine density functional theory (DFT) calculations and infrared reflection absorption spectroscopy (IRAS) to identify the structural motifs formed upon interaction of water with an atomically-defined Co\textsubscript{3}O\textsubscript{4}(111) surface. Three principal structures are observed: (i) strongly bound isolated OD, (ii) extended hydrogen-bonded OD/D\textsubscript{2}O structures, and (iii) a third structure which has not been reported to our knowledge. In this structure, surface Co\textsuperscript{2+} ions bind to three D\textsubscript{2}O molecules to form an octahedrally coordinated Co\textsuperscript{2+} with a “half hydration shell”. We propose that this hydration structure represents an important intermediate in re-organization and dissolution on oxide surfaces which expose highly unsaturated surface cations.

In this work, we scrutinize the interaction of water with Co\textsubscript{3}O\textsubscript{4}(111). Co\textsubscript{3}O\textsubscript{4} is an important material used in heterogeneous catalysis, electrocatalysis and photocatalysis as an active phase or a reducible support.\textsuperscript{12–20} However, only a few studies have been performed to understand its interaction with water at the molecular level (see e.g.\textsuperscript{12,13,20}). Comparing the interaction of water with Fe\textsubscript{3}O\textsubscript{4}(111) and Co\textsubscript{3}O\textsubscript{4}(111), the differences are dramatic. On Co\textsubscript{3}O\textsubscript{4}(111), water dissociates to form hydroxyl groups that reside up to high temperatures (570 K). Below 400 K, molecular and dissociated water coexist, giving rise to very characteristic but complex IR spectra.\textsuperscript{12–20} Although it is clear that the OD/D\textsubscript{2}O structures formed on Co\textsubscript{3}O\textsubscript{4}(111) are very different from those on Fe\textsubscript{3}O\textsubscript{4}(111), the nature of these structures has remained unknown.

Here, we identify the nature of these complex water structures by DFT and vibrational spectroscopy using a Co\textsubscript{3}O\textsubscript{4}(111) thin film with atomically defined surface structure (Figure 1). Besides the hydration networks, which are similar to those found on Fe\textsubscript{3}O\textsubscript{4}(111), we observe the phenomenon that has not been reported before: “local hydration” of a surface cation. Up to three D\textsubscript{2}O molecules adsorb on a single low-coordinated surface Co\textsuperscript{2+} ion, forming an octahedral ligand shell. Thus, a surface triaqua coordination complex is formed which appears as a hybrid between a hexaqua coordination complex in solution and a surface oxide cation. We believe that this “local hydration” plays an important role in structural transformations and dissolution processes at the oxide surface.

In our DFT calculations, we used a (2x2) supercell of a symmetric bulk-truncated 11-layer Co\textsubscript{3}O\textsubscript{4}(111) slab with structural parameters resembling the experimental ones (Figure 1).\textsuperscript{12} The surface contains Co\textsuperscript{2+} ions in C\textsubscript{3v} sites (labelled as Co\textsuperscript{3+}), O\textsuperscript{2–} ions directly surrounding Co\textsuperscript{2+} (O\textsubscript{adj}), and isolated O\textsuperscript{2–} ion (O\textsubscript{iso}) (Figure 1). Regarding the origin of OD, we adopt the notation from ref.\textsuperscript{12} and denote surface-derived hydroxyl as O\textsubscript{D} and water-derived hydroxyl as O\textsubscript{w}D.
To determine the OD structure, we calculated the adsorption energy of D$_2$O at various coverages (Table S2). At low coverage (<2.67 D$_2$O/nm$^2$), the favored configuration is a dissociated D$_2$O, generating a terminal O$_w$D and a tridentate O$_{adj}$D, only 0.07 eV more stable than the O$_w$D/O$_{iso}$D configuration (See section S5).

At higher coverage (>2.67 D$_2$O/nm$^2$), a new structure is found: 

![Figure 1. Surface IRRAS and isotopic labelling experiments for water on Co$_3$O$_4$(111): (a) schematic of the Co$_3$O$_4$(111) model systems and the experimental setup; (b) front and (c) side views of the structure model for the Co$_3$O$_4$(111) film grown on Ir(100).](image)

![Figure 2. Side and top views of the “half-solvated” Co$^{2+}$; symmetric (a1, a2) and slightly perturbed Co(D$_2$O)$_3$ cluster (b1, b2), predicted by DFT (Co$^{2+}$: green. Co$^{3+}$: blue O$^2$: red. H: white).](image)

Subsequent D$_2$O dissociates at free Co$^{2+}$, generating O$_w$D and O$_{adj}$D while slightly perturbing the Co(D$_2$O)$_3$ cluster. At even higher coverage (5.33 D$_2$O/nm$^2$ and above), an H-bonded network is formed (see Section S5). Since each surface O$_{iso}$ can only support one H-bond, the formation of a second Co(D$_2$O)$_3$ cluster adjacent to an existing one is inhibited. Structures exposing Co(D$_2$O)$_3$ clusters are predicted to be thermodynamically stable in a large temperature window around 300 K at the pressures applied in the experiments described below (Section S3). In summary, DFT predicts the formation of non-dissociated Co(D$_2$O)$_3$ clusters together with dissociated D$_2$O, linked through H-bonding at higher coverage.

To test the theoretical predictions, we have performed IRAS experiments (Figure 3). We used well-ordered Co$_3$O$_4$(111) films grown on an Ir(100) single crystal, as previously characterized by Heinz, Hammer and coworkers.$^{28,29}$ Initially, the Co$_3$O$_4$(111) films are free of hydroxyl groups and are terminated by a layer of tri-coordinated Co$^{2+}$ ions (Figure 1b).$^{12}$ This structure is identical to the one used in DFT.

To identify the nature of the water-derived species, we recorded IR spectra after exposure to D$_2$O and isotopically labelled D$_2$O$^{18}$O at different surface temperatures. The spectra for D$_2$O were recorded under D$_2$O pressure to prevent spontaneous back-exchange with non-labelled water from the background gas. In Figure 3, we compare the experimental spectra to calculated spectra from DFT (4.44 and 0.89 D$_2$O/nm$^2$, see SI).

At 500 K, the IR spectrum is dominated by a single sharp band around 2650 cm$^{-1}$ which can be assigned to isolated OD (see Figure 3b). In our previous work, we showed that these isolated hydroxyl groups are very stable and reside on the surface up to approximately 570 K.$^{12,20}$ However, the nature of the OD group could not be determined. To confirm the nature of the isolated OD, we compare the spectra
obtained with $^{18}$O-labelled and non-labelled D$_2$O (see Figure 3b). In both cases, we observe a sharp band between 2652 and 2656 cm$^{-1}$. The absence of any isotopic shift proves that the band originates from O$_{\text{ad}}$D (the isotopic shift between ν(D$^{16}$O) and ν(D$^{18}$O) is 17 cm$^{-1}$). Dissociation of D$_2$O should also yield an O$_{\text{ad}}$D group showing an isotopic shift for D$_2$$^{18}$O. However, we do not observe this species spectroscopically, most likely because the corresponding band is broadened and weaker, as this species is tilted with respect to the surface. Tilted vibrational modes are weakened because the metal surface selection rule (MSSR) also holds for thin oxide films on metals.\textsuperscript{30} In accordance with the experiment, the DFT calculations predict the formation of highly stable O$_{\text{iso}}$D through D$_2$O dissociation (Table S2). The calculated frequency of 2655 cm$^{-1}$ agrees with the experimental value, and the O$_{\text{iso}}$D group is oriented perpendicular to the surface, which leads to a large IR absorption signal. Therefore, we attribute the sharp IR band observed at 2655 cm$^{-1}$ to the O$_{\text{iso}}$D species.

Adsorption at 400K produces a complex spectrum (Figure 3a), with main features at 2728, 2667-2659 and 2545 cm$^{-1}$, and the calculated frequencies from DFT for intermediate water coverage (4.44 D$_2$O/nm$^2$) agree well with experimental ones (see Figure S1, Table S3). We attribute the most blue-shifted ν(O$_{\text{ad}}$D) band at 2728 cm$^{-1}$ to the slightly perturbed Co(D$_2$O)$_3$ cluster (Figure 2b) (DFT: 2727 cm$^{-1}$), while the most red-shifted band at 2545 cm$^{-1}$ is assigned to ν(O$_{\text{iso}}$D) (DFT: 2579, 2577 cm$^{-1}$). The experimentally observed isotopic shifts agree with this assignment. The bands
between 2667 and 2693 cm\(^{-1}\) are attributed to terminal O\(_{\text{w}}\)D and the remaining modes of the Co(D\(_2\))\(_3\) cluster (2715, 2698, 2693, 2678 cm\(^{-1}\)). They also show the expected isotopic shift. Finally, the band at 2659 cm\(^{-1}\) is assigned to residual O\(_{\text{iso}}\)D, like for the spectra at 500 K (no isotopic shift). No corresponding features were found by DFT for the weak O\(_{\text{w}}\)D bands at 2613 and 2630 cm\(^{-1}\); therefore, we tentative assign those to defects on the Co\(_3\)O\(_4\) film.

The nature of the spectrum changes with water coverage and the complexity of the experimental spectra suggest that several OD/D\(_2\)O structures with well-defined structural motifs coexist on the surface. This is not surprising, as DFT predicts different structures with similar energy (Table S2). Yet it is possible to identify three principal structures and their frequency ranges:

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**Figure 3.** (a1) surface IR spectra recorded during exposure of Co\(_3\)O\(_4\)(111) to D\(_2\)\(^{18}\)O and D\(_2\)\(^{16}\)O at a surface temperature of 370-400 K; (a2) corresponding vibrational modes calculated by DFT; (a3) peak assignments on the DFT model; (b1) surface IR spectra recorded at a surface temperature of 500 K; (b2) corresponding vibrational modes calculated by DFT, (b3) peak assignments on the DFT model.
(i) **$O_2D$ in extended OD/D$_2$O networks:** The bands in the range between 2680 and 2700 cm$^{-1}$ (showing isotopic shift) are attributed to free O$_2$D stretching modes of OD and D$_2$O in extended OD/D$_2$O networks.

(ii) **Isolated O$_2D$:** The features between 2650 and 2670 cm$^{-1}$ are attributed to isolated O$_2$D groups (O$_{iso}$D). The features can be differentiated from those in range (i) by the absence of an isotopic shift when adsorbing D$_2$O.

(iii) **Locally hydrated surface cations:** The high frequency band at 2730 cm$^{-1}$ is characteristic for free O$_2$D stretching modes of perturbed “half-hydrated” surface Co$_{2+}$ ions. In addition, these Co(O$_3$D)$_2$ clusters show some bands which overlap with region (i). All bands show the expected isotopic shifts when formed from D$_2$O.

The above assignment helps to understand the dramatic differences that are observed for water adsorption on Fe$_3$O$_4$(111) and Co$_3$O$_4$(111). The binding of both molecular and dissociated water are very different, leading to formation of a larger variety of structures even at low coverage. The most extreme case is the formation of Co(O$_3$D)$_3$ clusters. There are several factors that contribute to their stabilization on Co$_3$O$_4$(111) in contrast to Fe$_3$O$_4$(111). First, weaker electrostatic interactions near Co$_3^+$ centers as compared to the Fe$_3^+$ disfavors dissociative chemisorption on Co$_3$O$_4$(111). Further, the Co$_{2+}$ ion is larger than the Fe$_{3+}$, which, by rule-of-thumb, makes bonding near Fe$_{3+}$ appear more ionic. Paier et al. reported that D$_2$O dissociation over Fe$_{3+}$ releases ~0.145 eV, whereas we find a value of 0.10 eV on Co$_3$O$_4$(111) (Table S2). Finally, the newly formed octahedral coordination also contributes to the stabilization of the Co(O$_3$D)$_3$ cluster. The energy gain when forming Co(O$_3$D)$_3$ from to three isolated Co(D$_2$O) units is 0.16 eV/D$_2$O (Figure S3). The high T$_{2g}$ occupation of the octahedrally coordinated Co$_{2+}$ and the larger E$_g$-T$_{2g}$ splitting largely stabilizes the Co(O$_3$D)$_3$ complex over the tetrahedrally coordinated Co(O$_2$D) through additional ligand field stabilization energy (LFSE). On the other hand, no LFSE is gained by confining Fe$_{3+}$, a high spin $d^5$ ion, in an octahedral complex.

In conclusion, we have combined DFT calculations and surface IR spectroscopy with isotopically labelled water to identify the principal water and hydroxyl species that are formed upon adsorption and dissociation of water on an atomically-defined Co$_3$O$_4$(111) surface. We find that D$_2$O interacts strongly with pristine Co$_3$O$_4$(111), leading to formation of OD that are stable up to temperatures of 500 K and above. At lower temperature, OD groups coexist with molecular adsorbed D$_2$O, giving rise to a very complex IR spectrum. Three water-related species are found to coexist: (i) OD groups involving isolated surface O ions of the Co$_3$O$_4$(111) surface, (ii) extended partially dissociated OD/D$_2$O networks, and (iii) “half hydrated” surface Co$_{2+}$ ions, in which Co$_{2+}$ binds to three D$_2$O molecules, hence forming a hybrid structure between hexaaquacobalt in solution and surface oxide cation, with a octahedral coordination environment.

The “half hydrated” surface Co$_{2+}$ ions represent a new structural motif on an oxide surface which, so far, has not been observed experimentally or predicted theoretically. This motif is not observed on Fe$_3$O$_4$(111) because of electrostatic and electronic reasons. Our results further suggest that similar structures may be present on d$^8$ to d$^9$ transition metal cations on similar surfaces. We assume that the newly proposed structure represents an important intermediate in surface hydroxylation and hydrolysis of spinel surfaces and that our results will help to understand restructuring and dissolution phenomena on this important class of materials.

ASSOCIATED CONTENT

Supporting Information

Experimental and computational methods, details on vibrational modes and energies of adsorption.

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Notes
The authors declare no competing financial interests.

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REFERENCES


