

UCLA

UCLA Previously Published Works

Title

Water on Oxide Surfaces: A Triqua Surface Coordination Complex on Co₃O₄(111)

Permalink

<https://escholarship.org/uc/item/2j9108mc>

Journal

Journal of the American Chemical Society, 141(14)

ISSN

0002-7863

Authors

Yan, George
Wähler, Tobias
Schuster, Ralf
[et al.](#)

Publication Date

2019-04-10

DOI

10.1021/jacs.9b00898

Peer reviewed

Water on Oxide Surfaces: A Triqua Surface Coordination Complex on $\text{Co}_3\text{O}_4(111)$

George Yan[†], Tobias Wähler[‡], Ralf Schuster[‡], Matthias Schwarz[‡], Chantal Hohner[‡], Kristin Werner^{‡,§}, Jörg Libuda^{‡,||,*}, Philippe Sautet^{†,||,*}

[†] Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA, 90095, USA

[‡] Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany

^{||} Erlangen Catalysis Resource Center and Interdisciplinary Center for Interface-Controlled Processes, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

[§] Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA, 90095, USA

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 $\text{Co}_3\text{O}_4(111)$ surface. Three principal structures are observed: (i) strongly bound isolated OD, (ii) extended hydrogen-bonded OD/D₂O structures, and (iii) a third structure which has not been reported to our knowledge. In this structure, surface Co^{2+} ions bind to three D₂O molecules to form an octahedrally coordinated Co^{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.

The interaction of transition metal oxides with water heavily affects the stability and reactivity of these materials. Water can induce surface restructuring, phase transitions, sintering or dissolution, all important for heterogeneous catalysis and electrocatalysis.¹⁻⁷ Despite the pivotal importance of oxide/water interactions, it has been a long standing challenge to understand these processes at the atomic level.² Recently, sophisticated characterization techniques and theoretical analyses led to major breakthroughs. Researchers could identify structural motifs of molecular and dissociated water on several well-defined oxide surfaces at the atomic level.^{2,3,8-20} The interaction of Co_3O_4 and Fe_3O_4 surfaces with water is of high importance in water oxidation and water-gas shift catalysis.^{3,21} Water also affects the interaction between supported Au atoms and Fe_3O_4 .²² Water adsorption on Fe^{3+} terminated $\text{Fe}_3\text{O}_4(111)$ was investigated by Freund, Schauermann, Sauer, Paier, and coworkers.^{16,17,19} The authors identified OD/D₂O structures arranged as ordered overlayers which are weakly bound and desorb below 300 K.^{16,17,19}

In this work, we scrutinize the interaction of water with $\text{Co}_3\text{O}_4(111)$. Co_3O_4 is an important material used in heterogeneous catalysis, electrocatalysis and photocatalysis as an active phase or a reducible support.^{1,23-26} However, only a few studies have been performed to understand its interaction with water at the molecular level (see e.g.^{12,13,20}). Comparing the interaction of water with $\text{Fe}_3\text{O}_4(111)$ and $\text{Co}_3\text{O}_4(111)$, the differences are dramatic. On $\text{Co}_3\text{O}_4(111)$, 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.^{12,20} Although it is clear that the OD/D₂O structures formed on $\text{Co}_3\text{O}_4(111)$ are very different from those on $\text{Fe}_3\text{O}_4(111)$, 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 $\text{Co}_3\text{O}_4(111)$ thin film with atomically defined surface structure (Figure 1). Besides the hydration networks, which are similar to those found on $\text{Fe}_3\text{O}_4(111)$, we observe the phenomenon that has not been reported before: “local hydration” of a surface cation. Up to three D₂O molecules adsorb on a single low-coordinated surface Co^{2+} ion, forming an octahedral ligand shell. Thus, a surface triqua 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 $\text{Co}_3\text{O}_4(111)$ slab with structural parameters resembling the experimental ones (Figure 1).¹² The surface contains Co^{2+} ions in C_{3v} sites (labelled as Co^{2+}), O^{2-} ions directly surrounding Co^{2+} (O_{adj}), and isolated O^{2-} ion (O_{iso}) (Figure 1). Regarding the origin of OD, we adopt the notation from ref.¹⁷ and denote surface-derived hydroxyl as O_{sD} and water-derived hydroxyl as O_{wD} .

To determine the OD structure, we calculated the adsorption energy of D₂O at various coverages (Table S2). At low coverage (<2.67 D₂O/nm²), the favored configuration is a dissociated D₂O, generating a terminal O_wD and a tridentate O_{adj}D, only 0.07 eV more stable than the O_wD/O_{iso}D configuration (See section S5).

At higher coverage (>2.67 D₂O/nm²), a new structure is found:

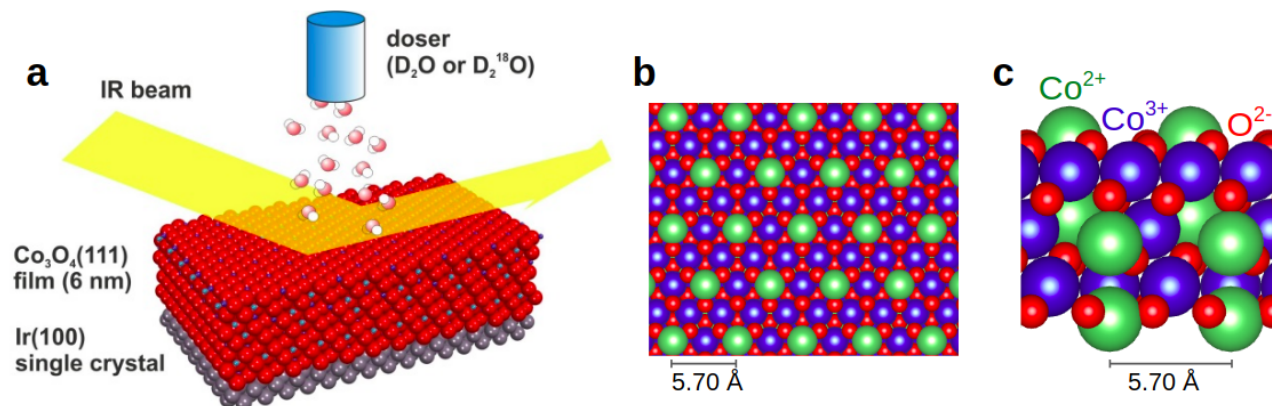


Figure 1. Surface IRRAS and isotopic labelling experiments for water on Co₃O₄(111): (a) schematic of the Co₃O₄(111) model systems and the experimental setup; (b) front and (c) side views of the structure model for the Co₃O₄(111) film grown on Ir(100).

surprisingly, the three D₂O molecules in a unit cell prefer to stay non-dissociated and bind to a single Co²⁺ surface ion (Figure 2a). The Co²⁺ is now surrounded by an octahedral ligand shell, resembling a “half-solvated” triaquo Co²⁺ ion. This local arrangement will be referred to as “Co(D₂O)₃ cluster”.²⁷ The effects of Co(D₂O)₃ formation on the substrate are minor, with only a slight elevation of that Co²⁺ center (+0.1 Å) and small spin densities occurring on the neighboring Co³⁺. Structures in which D₂O molecules in the cluster are all or partially dissociated are less stable; however, the energy differences are small, and coexistence of these different structures is expected at higher temperature, assuming that the formation of isomers follows a Boltzmann distribution (SI).

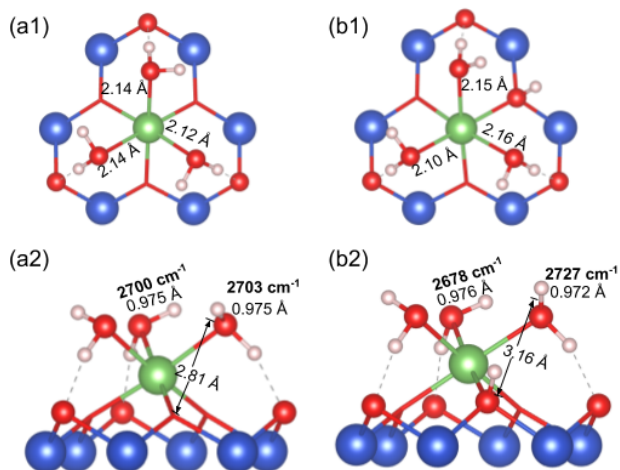


Figure 2. Side and top views of the “half-solvated” Co²⁺: symmetric (a1, a2) and slightly perturbed Co(D₂O)₃ cluster (b1, b2), predicted by DFT (Co²⁺: green, Co³⁺: blue, O²⁻: red, H: white).

Subsequent D₂O dissociates at free Co²⁺, generating O_wD and O_{adj}D while slightly perturbing the Co(D₂O)₃ cluster. At even higher coverage (5.33 D₂O/nm² 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(D₂O)₃ cluster adjacent to an existing one is inhibited. Structures exposing Co(D₂O)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(D₂O)₃ clusters together with dissociated D₂O, linked through H-bonding at higher coverage.

To test the theoretical predictions, we have performed IRAS experiments (Figure 3). We used well-ordered Co₃O₄(111) films grown on an Ir(100) single crystal, as previously characterized by Heinz, Hammer and coworkers.^{28,29} Initially, the Co₃O₄(111) films are free of hydroxyl groups and are terminated by a layer of tri-coordinated Co²⁺ 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 D₂¹⁶O and isotopically labelled D₂¹⁸O at different surface temperatures. The spectra for D₂¹⁸O were recorded under D₂¹⁸O 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 D₂O/nm², 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_2O (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_sD (the isotopic shift between $\nu(\text{D}^{16}\text{O})$ and $\nu(\text{D}^{18}\text{O})$ is 17 cm^{-1}). Dissociation of D_2O should also yield an O_wD 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.³⁰ In accordance with the experiment, the DFT calculations predict the formation of highly stable $\text{O}_{\text{iso}}\text{D}$ through D_2O dissociation (Table S2). The calculated frequency of 2655 cm^{-1} agrees with the experimental value, and the $\text{O}_{\text{iso}}\text{D}$ 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 $\text{O}_{\text{iso}}\text{D}$ 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 $\text{D}_2\text{O}/\text{nm}^2$) agree well with experimental ones (see Figure S1, Table S3). We attribute the most blue-shifted $\nu(\text{O}_w\text{D})$ band at 2728 cm^{-1} to the slightly perturbed $\text{Co}(\text{D}_2\text{O})_3$ cluster (Figure 2b) (DFT: 2727 cm^{-1}), while the most red-shifted band at 2545 cm^{-1} is assigned to $\nu(\text{O}_{\text{adj}}\text{-D})$ (DFT: 2579, 2577 cm^{-1}). The experimentally observed isotopic shifts agree with this assignment. The bands

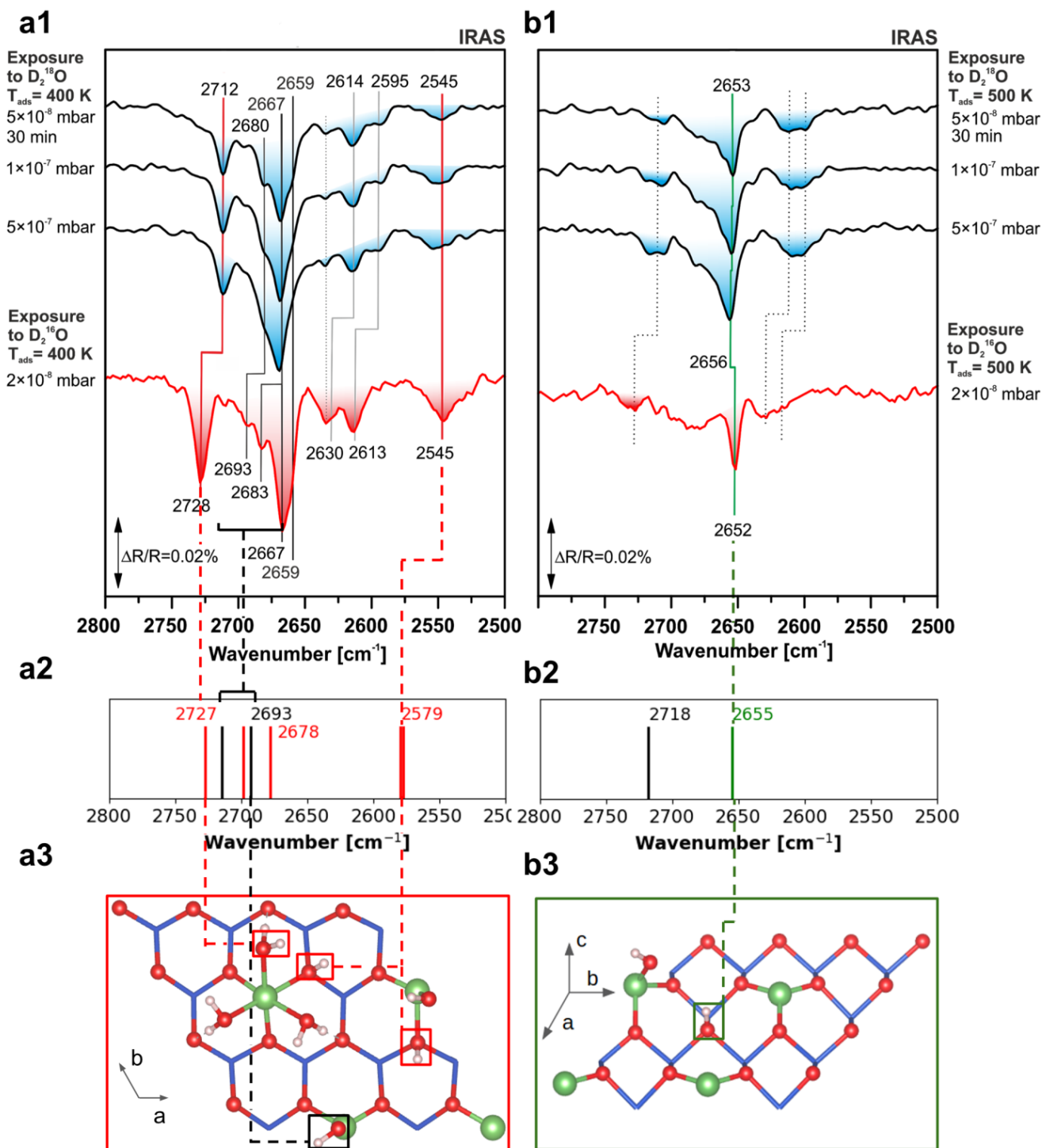


Figure 3. (a1) surface IR spectra recorded during exposure of $\text{Co}_3\text{O}_4(111)$ to D_2^{18}O and D_2^{16}O at a surface temperature of 370–400 K; (a2) corresponding vibrational modes calculated by DFT; (a3) peak assignments on the DFT model; (b1) surface IR spectra recorded at a surface temperature of 500 K; (b2) corresponding vibrational modes calculated by DFT, (b3) peak assignments on the DFT model.

between 2667 and 2693 cm^{-1} are attributed to terminal O_{wD} and the remaining modes of the $\text{Co}(\text{D}_2\text{O})_3$ 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_{isoD} , like for the spectra at 500 K (no isotopic shift). No corresponding features were found by DFT for the weak O_{wD} bands at 2613 and 2630 cm^{-1} ; therefore, we tentatively assign those to defects on the Co_3O_4 film.

The nature of the spectrum changes with water coverage and the complexity of the experimental spectra suggest that several OD/ D_2O 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:

- (i) ***O_wD in extended OD/D₂O networks:*** The bands in the range between 2680 and 2700 cm⁻¹ (showing isotopic shift) are attributed to free O_wD stretching modes of OD and D₂O in extended OD/D₂O networks.
- (ii) ***Isolated O_sD:*** The features between 2650 and 2670 cm⁻¹ are attributed to isolated O_sD groups (O_{iso}D). The features can be differentiated from those in range (i) by the absence of an isotopic shift when adsorbing D₂¹⁸O
- (iii) ***Locally hydrated surface cations:*** The high frequency band at 2730 cm⁻¹ is characteristic for free O_wD stretching modes of perturbed “half-hydrated” surface Co²⁺ ions. In addition, these Co(D₂O)₃ clusters show some bands which overlap with region (i). All bands show the expected isotopic shifts when formed from D₂¹⁸O. The Co(D₂O)₃ clusters involve H-bonding to O_{iso}. Formation of perturbed Co(D₂O)₃ are accompanied by O_{adj}D species which give rise to strongly red-shifted band around 2550 cm⁻¹ (showing no isotopic shift)

The above assignment helps to understand the dramatic differences that are observed for water adsorption on Fe₃O₄(111) and Co₃O₄(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(D₂O)₃ clusters. There are several factors that contribute to their stabilization on Co₃O₄(111) in contrast to Fe₃O₄(111). First, weaker electrostatic interactions near Co²⁺ centers as compared to the Fe³⁺ disfavors dissociative chemisorption on Co₃O₄(111). Further, the Co²⁺ ion is larger than the Fe³⁺, which, by rule-of-thumb, makes bonding near Fe³⁺ appear more ionic.³¹ Paier et al. reported that D₂O dissociation over Fe³⁺ releases ~0.145 eV, whereas we find a value of 0.10 eV on Co₃O₄(111) (Table S2).¹⁶ Finally, the newly formed octahedral coordination also contributes to the stabilization of the Co(D₂O)₃ cluster. The energy gain when forming Co(D₂O)₃ from to three isolated Co(D₂O) units is 0.16 eV/D₂O (Figure S3). The high T_{2g} occupation of the octahedrally coordinated Co²⁺ and the larger E_g-T_{2g} splitting largely stabilizes the Co(D₂O)₃ complex over the tetrahedrally coordinated Co(O_wD) through additional ligand field stabilization energy (LFSE).³² On the other hand, no LFSE is gained by confining Fe³⁺, a high spin d⁵ ion,³³ 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 Co₃O₄(111) surface. We find that D₂O interacts strongly with pristine Co₃O₄(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 D₂O, 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 Co₃O₄(111) surface, (ii) extended partially dissociated OD/D₂O networks, and (iii) “half hydrated” surface Co²⁺ ions, in which Co²⁺ binds to three D₂O molecules, hence forming a hybrid structure between hexaaquacobalt in solution and surface oxide cation, with a octahedral coordination environment.

The “half hydrated” surface Co²⁺ 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 Fe₃O₄(111) because of electrostatic and electronic reasons. Our results further suggest that similar structures may be present on d⁶ to d⁸ transition metal cations on similar surfaces.³⁴⁻³⁵ 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.

AUTHOR INFORMATION

Corresponding Authors

Jörg Libuda: joerg.libuda@fau.de
Philippe Sautet: sautet@ucla.edu

Present Addresses

§: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Chemische Physik, Faradayweg 4-6, 14195 Berlin

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This project was financially supported by Deutsche Forschungsgemeinschaft with the Research Unit FOR 1878 ‘funCOS’ and further projects and by UCLA Samueli School of Engineering (startup funds of PS). Additional support by the Excellence Cluster ‘Engineering of Advanced Materials’ is acknowledged. The calculations in this work used computational and storage services associated with the Hoffman2 shared computational cluster located at UCLA, provided by UCLA’s Institute for Digital Research and Education Group (IDRE). This work also used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1548562. Specifically, it used the Bridges system, which is supported by NSF award number ACI-1445606, at the Pittsburgh Supercomputing Center (PSC).^{36,37}

REFERENCES

- (1) Xie, X.; Li, Y.; Liu, Z. Q.; Haruta, M.; Shen, W. Low-Temperature Oxidation of CO Catalysed by Co₃O₄ Nanorods. *Nature* **2009**, 458 (7239), 746–749.
- (2) Doyle, R. L.; Godwin, I. J.; Brandon, M. P.; Lyons, M. E. G. Redox and Electrochemical Water Splitting Catalytic Properties of Hydrated Metal Oxide Modified Electrodes. *Phys. Chem. Chem. Phys.* **2013**, 15, 13737–13783.
- (3) Parkinson, G. S. Iron Oxide Surfaces. *Surf. Sci. Rep.* **2016**, 71 (1), 272–365.
- (4) Mu, R.; Zhao, Z.-J.; Dohnalek, Z.; Gong, J. Structural Motifs of Water on Metal Oxide Surfaces. *Chem. Soc. Rev.* **2017**, 46, 1785–1806.
- (5) Faisal, F.; Stumm, C.; Bertram, M.; Waidhas, F.; Lykhach, Y.; Cherevko, S.; Xiang, F.; Ammon, M.; Vorokhta, M.; Šmíd, B.; Skála, T.; Tsud, N.; Neitzel, A.; Beranová, K.; Prince, K. C.; Geiger, S.; Kasian, O.; Wähler, T.; Schuster, R.; Schneider, M.

- A.; Matolín, V.; Mayrhofer, K. J. J.; Brummel, O.; Libuda, J. Electrifying Model Catalysts for Understanding Electrocatalytic Reactions in Liquid Electrolytes. *Nat. Mater.* **2018**, *17* (7), 592–598.
- (6) Fester, J.; García-Melchor, M.; Walton, A. S.; Bajdich, M.; Li, Z.; Lammich, L.; Vojvodic, A.; Lauritsen, J. V. Edge Reactivity and Water-Assisted Dissociation on Cobalt Oxide Nanoislands. *Nat. Commun.* **2017**, *8*, 6–13.
- (7) Parkinson, G. S.; Novotný, Z.; Jacobson, P.; Schmid, M.; Diebold, U. Room Temperature Water Splitting at the Surface of Magnetite. *J. Am. Chem. Soc.* **2011**, *133* (32), 12650–12655.
- (8) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (9) Włodarczyk, R.; Sierka, M.; Kwapien, K.; Sauer, J.; Carrasco, E.; Aumer, A.; Gomes, J. F.; Sterrer, M.; Freund, H. J. Structures of the Ordered Water Monolayer on MgO(001). *J. Phys. Chem. C* **2011**, *115* (14), 6764–6774.
- (10) Chizallet, C.; Costentin, G.; Che, M.; Delbecq, F.; Sautet, P. Revisiting Acido-Basicity of the MgO Surface by Periodic Density Functional Theory Calculations: Role of Surface Topology and Ion Coordination on Water Dissociation. *J. Phys. Chem. B* **2006**, *110* (32), 15878–15886.
- (11) Chizallet, C.; Costentin, G.; Che, M.; Delbecq, F.; Sautet, P. Infrared Characterization of Hydroxyl Groups on MgO: A Periodic and Cluster Density Functional Theory Study. *J. Am. Chem. Soc.* **2007**, *129* (20), 6442–6452.
- (12) Schwarz, M.; Faisal, F.; Mohr, S.; Hohner, C.; Werner, K.; Xu, T.; Skála, T.; Tsud, N.; Prince, K. C.; Matolín, V.; Lykhach, Y.; Libuda, J. Structure-Dependent Dissociation of Water on Cobalt Oxide. *J. Phys. Chem. Lett.* **2018**, *9*, 2763–2769.
- (13) Pettito, S. C.; Marsh, E. M.; Carson, G. A.; Langell, M. A. Cobalt Oxide Surface Chemistry: The Interaction of CoO(100), Co₃O₄(110) and Co₃O₄(111) with Oxygen and Water. *J. Mol. Catal. A Chem.* **2008**, *281*, 49–58.
- (14) Chen, J.; Selloni, A. Water Adsorption and Oxidation at the Co₃O₄ (110) Surface. *J. Phys. Chem. Lett.* **2012**, *3* (19), 2808–2814.
- (15) Selcuk, S.; Selloni, A. DFT+U Study of the Surface Structure and Stability of Co₃O₄(110): Dependence on U. *J. Phys. Chem. C* **2015**, *119* (18), 9973–9979.
- (16) Zaki, E.; Mirabella, F.; Ivars-Barceló, F.; Seifert, J.; Carey, S.; Shaikhutdinov, S.; Freund, H.-J.; Li, X.; Paier, J.; Sauer, J. Water Adsorption on the Fe₃O₄(111) Surface: Dissociation and Network Formation. *Phys. Chem. Chem. Phys.* **2018**, *122* (2), 721–729.
- (17) Mirabella, F.; Zaki, E.; Ivars-Barceló, F.; Li, X.; Paier, J.; Sauer, J.; Shaikhutdinov, S.; Freund, H. J. Cooperative Formation of Long-Range Ordering in Water Ad-Layers on Fe₃O₄(111) Surfaces. *Angew. Chemie - Int. Ed.* **2018**, *57* (5), 1409–1413.
- (18) Herman, G. S.; Dohnalek, Z.; Ruzycski, N.; Diebold, U. Experimental Investigation of the Interaction of Water and Methanol with Anatase-TiO₂(101). *J. Phys. Chem. B* **2003**, *107*, 2788–2795.
- (19) Dementyev, P.; Dostert, K.-H.; Ivars-Barceló, F.; O'Brien, C. P.; Mirabella, F.; Schauer mann, S.; Li, X.; Paier, J.; Sauer, J.; Freund, H.-J. Water Interaction with Iron Oxides. *Angew. Chemie Int. Ed.* **2015**, *54* (47), 13942–13946.
- (20) Schwarz, M.; Mohr, S.; Hohner, C.; Werner, K.; Xu, T.; Libuda, J. Water on Atomically-Defined Cobalt Oxide Surfaces Studied by Temperature-Programmed IR Reflection Absorption Spectroscopy and Steady State Isotopic Exchange. *J. Phys. Chem. C* **2018**, *acs.jpcc.8b04611*.
- (21) Bajdich, M.; García-Mota, M.; Vojvodic, A.; Nørskov, J. K.; Bell, A. T. Theoretical Investigation of the Activity of Cobalt Oxides for the Electrochemical Oxidation of Water. *J. Am. Chem. Soc.* **2013**, *135* (36), 13521–13530.
- (22) Rim, K. T.; Eom, D.; Chan, S.-W.; Flytzani-Stephanopoulos, M.; Flynn, G. W.; Wen, X.-D.; Batista, E. R. Scanning Tunneling Microscopy and Theoretical Study of Water Adsorption on Fe₃O₄: Implications for Catalysis. *J. Am. Chem. Soc.* **2012**, *134* (46), 18979–18985.
- (23) Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co₃O₄ Nanocrystals on Graphene as a Synergistic Catalyst for Oxygen Reduction Reaction. *Nat. Mater.* **2011**, *10* (10), 780–786.
- (24) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; G., M. J.; Delmon, B. Low-Temperature Oxidation of CO over Gold Supported TiO₂, Alpha-Fe₂O₃, and Co₃O₄. *J. Catal.* **1993**, *144*, 175–192.
- (25) Ren, Y.; Ma, Z.; Qian, L.; Dai, S.; He, H.; Bruce, P. G. Ordered Crystalline Mesoporous Oxides as Catalysts for CO Oxidation. *Catal. Letters* **2009**, *131* (1–2), 146–154.
- (26) Sun, S.; Sun, L.; Xi, S.; Du, Y.; Anu Prathap, M. U.; Wang, Z.; Zhang, Q.; Fisher, A.; Xu, Z. J. Electrochemical Oxidation of C₃ Saturated Alcohols on Co₃O₄ in Alkaline. *Electrochim. Acta* **2017**, *228*, 183–194.
- (27) Ohtaki, H.; Radnai, T. Structure and Dynamics of Hydrated Ions. *Chem. Rev.* **1993**, *93*, 1157–1204.
- (28) Heinz, K.; Hammer, L. Epitaxial Cobalt Oxide Films on Ir(100)—the Importance of Crystallographic Analyses. *J. Phys. Condens. Matter* **2013**, *25* (17), 173001.
- (29) Meyer, W.; Biedermann, K.; Gubo, M.; Hammer, L.; Heinz, K. Surface Structure of Polar Co₃O₄(111) Films Grown Epitaxially on Ir(100)-(1×1). *J. Phys. Condens. Matter* **2008**, *20*, 265011.
- (30) Hoffmann, F. M. Infrared Reflection-Absorption Spectroscopy of Adsorbed Molecules. *Surf. Sci. Rep.* **1993**, *3*, 109.
- (31) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr.* **1976**, *A32*, 751.
- (32) Roth, W. L. The Magnetic Structure of Co₃O₄. *J. Phys. Chem. Solids* **1964**, *25* (1), 1–10.
- (33) Yu, X.; Huo, C.-F.; Li, Y.-W.; Wang, J.; Jiao, H. Fe₃O₄ Surface Electronic Structures and Stability from GGA+U. *Surf. Sci.* **2012**, *606*, 872–879.
- (34) Yu, X.; Tian, X.; Wang, S. Adsorption of Ni, Pd, Pt, Cu, Ag and Au on the Fe₃O₄(111) Surface. *Surf. Sci.* **2014**, *628*, 141–147.
- (35) Fu, Z.; Yang, B.; Zhang, Y.; Zhang, N.; Yang, Z. Dopant Segregation and CO Adsorption on Doped Fe₃O₄(111) Surfaces: A First-Principle Study. *J. Catal.* **2018**, *364*, 291–296.
- (36) Towns, J.; Cockerill, T.; Dahan, M.; Foster, I.; Gauthier, K.; Grimshaw, A.; Hazlewood, V.; Lathrop, S.; Lifka, D.; Peterson, G. D.; Roskies, R.; Scott, J. R.; Wilkens-Diehr, N. XSEDE: Accelerating Scientific Discovery. *Comput. Sci. Eng.* **2014**, *16* (5), 62–74.
- (37) Nystrom, N. A.; Levine, M. J.; Roskies, R. Z.; Scott, J. R. Bridges: A Uniquely Flexible HPC Resource for New Communities and Data Analytics. In *Proceedings of the 2015 XSEDE Conference: Scientific Advancements Enabled by Enhanced Cyberinfrastructure*, St. Louis, Missouri, USA, July 26–30, 2015; ACM: New York, NY, USA, **2015**; p 30.

TOC Graphic

