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Interfacial Reactions of Tetraphenylporphyrin with Cobalt-Oxide Thin Films

Daniel Wechsler[a], Cynthia C. Fernández[b], Quratulain Tariq[a], Nataliya Tsud[c], Kevin C. Prince[c, d], Federico J. Williams[a, b], Hans-Peter Steinrück[a], and Ole Lytken[a]*

Abstract: We have studied the adsorption and interfacial reactions of 2H-tetraphenylporphyrin (2HTPP) with cobalt-terminated Co_3O_4(111) and oxygen-terminated CoO(111) thin films using synchrotron-radiation X-ray photoelectron spectroscopy. Already at 275 K, we find evidence for the formation of a metalated species, most likely CoTPP, on both surfaces. The degree of self-metalation increases with temperature on both surfaces until 475 K, where the metalation is almost complete. At 575 K the porphyrin coverage decreases drastically on the reducible cobalt-terminated Co_3O_4(111) surface, while higher temperatures are needed on the non-reducible oxygen-terminated CoO(111). The low temperature self-metalation is similar to that observed on MgO(100) surfaces, but drastically different from that observed on TiO_2(110), where no self-metalation is observed at room temperature.

Introduction

Organic macrocycles containing porphyrin functionalities have a ubiquitous role in nature where they play an important part in several processes. Remarkable examples are oxygen transport and storage in hemoglobin and myoglobin[1], electron transport in cytochrome c[2] and light harvesting in chlorophyll[3]. A broad range of functions is possible as the electronic, optical and chemical properties can be tuned by the choice of the metal ion at the center of the macrocycle. Furthermore, different chemical functionalities can be incorporated into the periphery of the macrocycle serving, for instance, as anchoring groups on different substrates. Porphyrin molecules attached to solid surfaces are therefore relevant for molecular devices including gas sensors[4-5], organic light emitting devices[6], catalysts[7] and photovoltaic cells[8-10]. In many of these systems, the porphyrin molecules are attached to oxide substrates, which makes fundamental studies on the adsorption and interaction of porphyrin molecules with oxide surfaces important.

Recent research effort was devoted to gain understanding of the porphyrin/oxide interface[11-19]. Adsorption of free-base porphyrin molecules on both oxide[12-14, 18] and metal[20-24] surfaces can result in the incorporation of substrate metal atoms into the center of the macrocycle, i.e. in self-metalation. For metal surfaces self-metalation proceeds via a redox process, where a metal atom is oxidized and incorporated into the macrocycle ring and the H atoms attached to the aminic nitrogen atoms in the molecule are reduced to H_2[21, 23]. If oxygen is present on a metal surface, the rate of metalation can be increased. This is probably because the abstracted hydrogen atoms can be stabilized by the oxygen and form hydroxyl groups[25]. Self-metalation on oxide substrates, on the other hand, is proposed to take place via an ion-exchange reaction,[12-13] where a metal cation from the oxide surface is incorporated into the center of the macrocycle whilst two protons are released from the aminic nitrogen atoms. Porphyrin molecules deposited onto oxide substrates can also undergo a protonation reaction[11] where the iminic nitrogen atoms at the macrocycle core capture protons presumably from surface hydroxyl groups. This proton-exchange reaction results in the formation of a temperature-stable doubly-protonated porphyrin-diacid species on TiO_2(110) surfaces[11] which hinders self-metalation[12]. Therefore, the accessibility of surface metal cations and surface hydroxyl groups should be a key factor controlling the self-metalation and proton-exchange reactions. In this context, studying the interaction of free-base porphyrin molecules with cobalt oxide thin films is particularly attractive due to the possibility of tuning the chemical nature of the substrate topmost layer with ease[26].

In this work, we have used synchrotron X-ray photoelectron spectroscopy (XPS) to study the adsorption and interfacial reactions of tetraphenyl porphyrin (2HTPP) deposited on

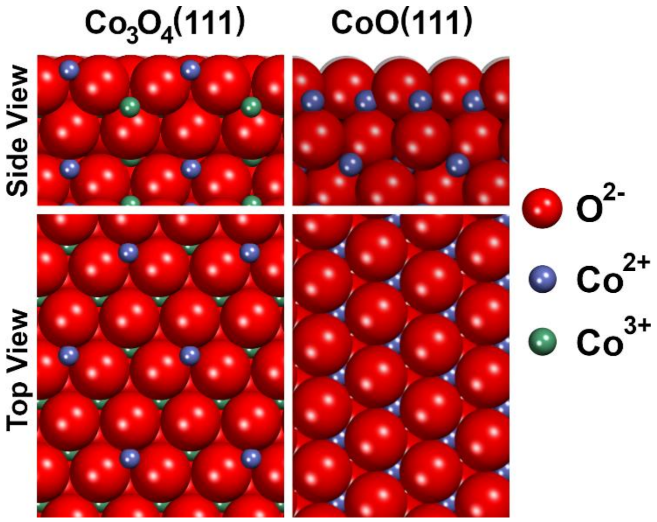

Figure 1. Model of Co_3O_4(111) (left) and CoO(111) (right).[26]

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[a] D. Wechsler, Q. Tariq, Prof. Dr. F. J. Williams, Prof. Dr. H.-P. Steinrück, Dr. O. Lytken
Chair of Physical Chemistry II, University Erlangen-Nürnberg
Egerlandstraße 3, 91058 Erlangen, Germany
E-mail: ole.lytken@fau.de
[b] C. C. Fernández, F. J. Williams
Departamento de Química Inorgánica, Analítica y Química Física,
Facultad de Ciencias Exactas y Naturales, INQUIMAE-CONICET
Universidad de Buenos Aires
Pabellón 2, Buenos Aires C1428EHA, Argentina
[c] N. Tsud, K. C. Prince
Elettra-Sincrotrone Trieste S.C.p.A.
Strada Statale 14, km 163.5, 34149 Basovizza-Trieste, Italy
[d] K. C. Prince
IOM, Strada Statale 14, km 163.5, 34149 Basovizza-Trieste, Italy

Co_3O_4(111) and CoO(111) thin films[27]. Co_3O_4(111) thin films expose threefold coordinated Co^{2+} ions in the topmost layer, whereas polar CoO(111) thin films are terminated by O^{2-} ions, while the fourfold coordinated Co^{2+} ions are recessed below the surface. Hence, both films have the Co^{2+} ions needed for self-metalation to take place, however, only Co_3O_4(111) have Co^{2+} available in the topmost layer.

Results and Discussion

The top spectrum in Figure 2 shows the N 1s XPS spectrum measured after the adsorption of 2HTPP multilayers (5 ML) on Co_3O_4(111) at 275 K. The spectrum has two main peaks (fitted in green) of equal intensity due to the two aminic (–NH–, 400.0 eV) and two iminic (–N=, 398.0 eV) nitrogen atoms present in the free-base porphyrin molecule[30-32]. Also present are two shake-up satellite peaks (fitted in blue) which are typically observed in porphyrin multilayer spectra[20]. When instead only 0.9 ML 2HTPP is deposited, a new feature appears at 398.7 eV (fitted in red), consistent with metalated CoTPP molecules. The same feature also appears when 2HTPP is deposited on CoO(111), indicating similar degrees of metalation on both cobalt-oxide surfaces. In fact, the two spectra look almost identical.

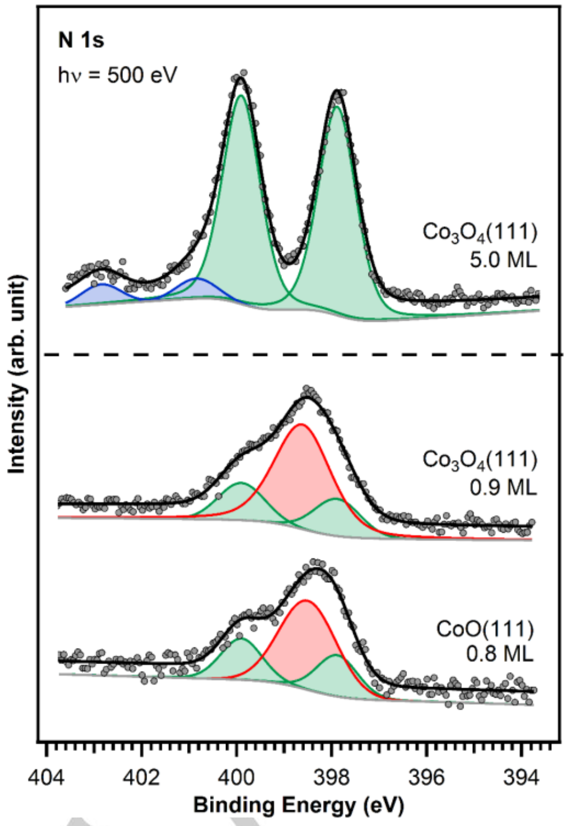

Figure 2. N 1s XPS spectra of 5.0 and 0.9 ML of 2HTPP on Co_3O_4(111) and 0.8 ML on CoO(111) at 275 K. Green peaks represent the free-base porphyrin and the red peak is attributed to the metalloporphyrin species. Blue peaks are shake-up satellites.

The formation of CoTPP can happen through the incorporation of the Co^{2+} ions present in both Co_3O_4 and CoO into the 2HTPP molecule. Such self-metalation reactions have previously been reported on both metal[20, 24, 33] and oxide[11, 13-14] surfaces. The behavior we observe on Co_3O_4(111) and on CoO(111) is very similar to that previously observed by Schneider *et al.*[13] on MgO(100), where adsorption of 2HTPP at 300 K resulted in 50% metalation to MgTPP. DFT calculations[13] have shown that the self-metalation reaction on MgO(100) is most likely occurring at corners, edges or steps. This could explain why we observe almost identical behaviors on both cobalt–oxide surfaces, despite the fact that the cobalt ions should be less accessible on the oxygen-terminated CoO(111) surface;[26] The terraces might be different, but the steps and defect could be very similar.

Figure 3 shows the thermal evolution of the self-metalation reaction on the two cobalt-oxide surfaces as 0.8 and 0.9 ML 2HTPP are heated to 775 K. On both surfaces the degree of metalation increases with increasing temperature until 475 K at which point the reaction is almost complete. Above 475 K a small, new feature appears at 397.0 eV (brown peak). We attribute this to a decomposition of the porphyrin molecules. Increasing the temperature further leads to an abrupt loss of molecules on both surfaces, but the temperature at which this happens is very different for the two surfaces. On the reducible Co_3O_4(111) surface the porphyrin molecules disappear completely from the surface between 575 and 625 K, whereas an additional 150 K is needed before the same happens on CoO(111). The loss of molecules is corroborated by the C 1s core-level region (not shown), which exhibits a loss identical to the N 1s region. We believe what happens at 625 K on Co_3O_4(111) is that the molecules are burned away by oxygen pulled from the surface, reducing the Co_3O_4 surface to CoO. This is supported by Co 2p core-level spectra of the Co_3O_4(111) surface after annealing to 675 K, see Figure 4. The satellite structure of Co_3O_4 and CoO are markedly different and allows the two to be differentiated,[34] and after the porphyrin-covered Co_3O_4(111) surface is annealed to 675 K the satellite structure clearly begin to the resemble that of CoO(111), see Figure 4, indicating a reduction of the surface. This is in agreement with findings by Heinz and Hammer[26]: Depending on the thickness of the oxide Co_3O_4(111) converts to CoO(111) between 500 to 600 K under the release of oxygen.

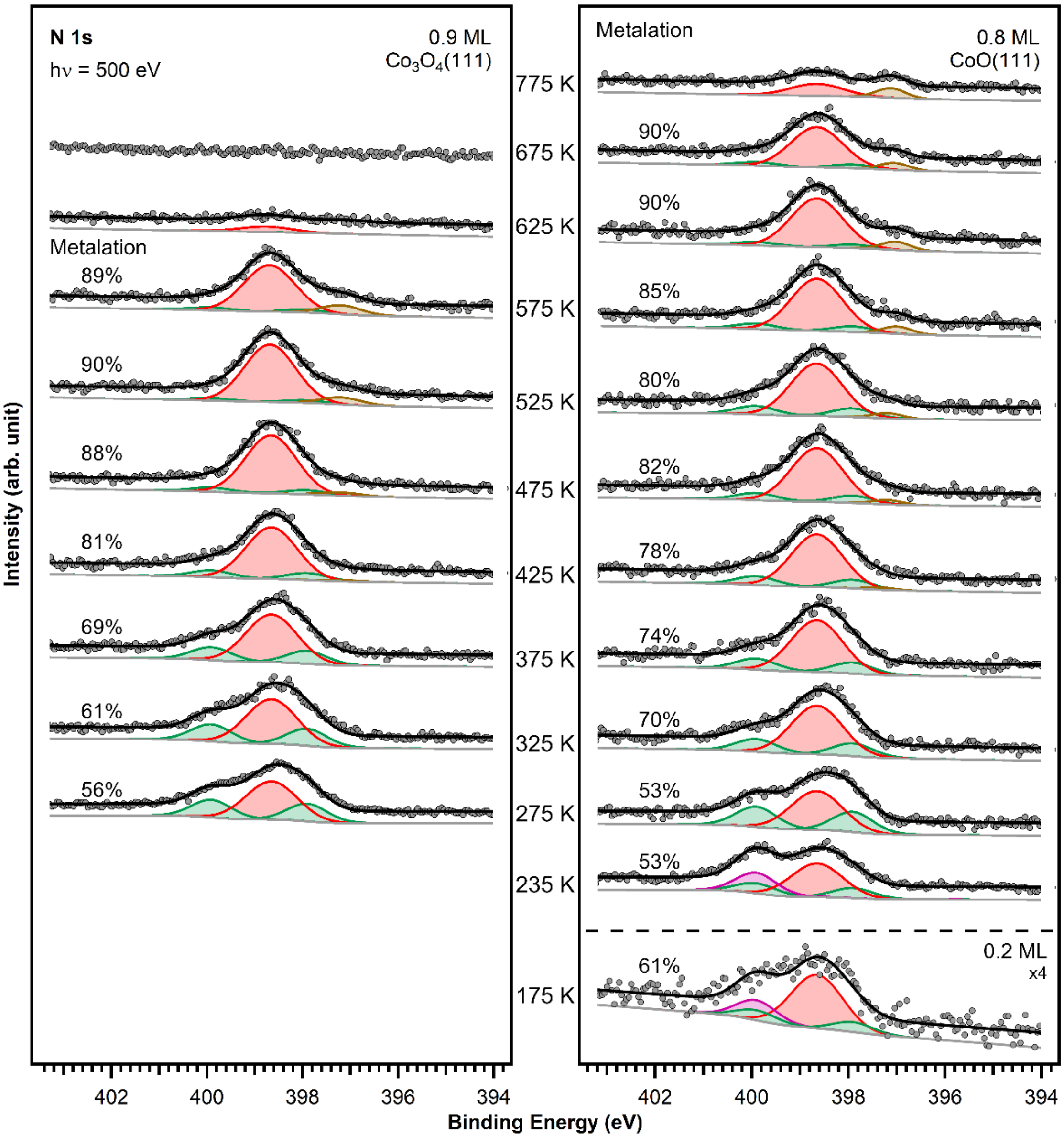

Figure 3. N 1s spectra of submonolayer coverages of 2HTPP on $Co_3O_4(111)$ (left) and CoO(111) (right) heated in 50 K steps, 10 minutes per step, to 775 K. Green peaks represent the free-base porphyrin molecules, protonated porphyrins give rise to the violet peaks and the red peaks are attributed to the metalloporphyrin species. Brown peaks are decomposition products at higher temperatures.

On CoO(111) we did additional measurements below 275 K, see Figure 3, and we observe partial metalation even at 175 K. When comparing the temperature range, we observe for metalation with similar measurements on other metal[22] and oxide surfaces[12, 14], one finds that the temperature range is rather large in the present case. One possible explanation is that metalation requires diffusion of molecule to and from defect sites, but as the coverage is increased above 0.5 ML the density of molecules on the surface prevents easy diffusion and much higher temperatures are needed to metalate the remaining molecules.

Below 275 K an additional feature (violet peak) at the position of the aminic nitrogen atoms (–NH–, 400.0 eV) appears in the N 1s spectra, see Figure 3. This feature has previously been observed for 2HTPP on TiO_2 (110) and was assigned to a protonation of the iminic nitrogen atoms of the porphyrin macrocycle, presumably with surface hydroxyl groups, forming a porphyrin diacid molecule.[11-12] The behavior of the protonated porphyrin molecules on CoO(111) is very different from that on $TiO_2(110)$: On $TiO_2(110)$ at submonolayer coverages 2HTPP is fully protonated into the diacid form. The diacid species is also very temperature-stable on $TiO_2(110)$ and metalates only at significantly higher temperatures than free-base 2HTPP.[12]

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On CoO(111) in contrast we only observe about 50% protonation of the unmetalated 2HTPP molecules, see Figure 3. In addition, heating to 275 K converts the protonated species completely into free-base 2HTPP without changing the degree of self-metalation, even though surface –OH groups are stable up to more than 450 K on CoO(111).[27] Given that water molecules are known to desorb from cobalt oxide surfaces at around 250 K,[27,35] we propose that molecularly adsorbed water from the background of the UHV chamber is responsible for the protonation we observe on CoO(111) at 235 K and below. Upon heating to 275 K the reaction is reversible, the porphyrin molecules deprotonate, water desorbs, and only free-base molecules remain on the surface.

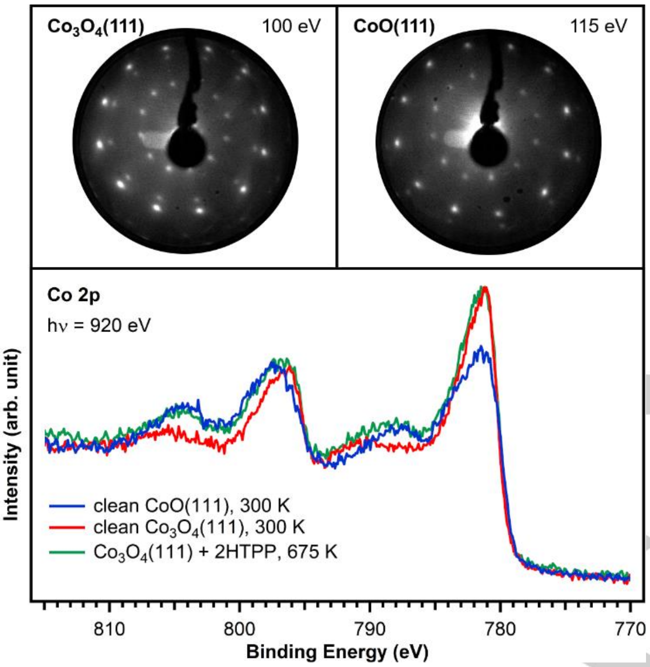

Figure 4. LEED diffraction patterns and Co 2p spectra of clean CoO(111) and Co_3O_4(111) at room temperature and of Co_3O_4(111) with adsorbed 2HTPP after annealing to 675 K.

Conclusions

In conclusion the behavior of 2HTPP on Co_3O_4(111) and CoO(111) is very similar to that of 2HTPP on MgO(100), see Figure 5: At room temperature half the molecules metalate on all three surfaces, and no protonation of the remaining free-base 2HTPP is observed. Room temperature metalation could be a general trend for oxide surfaces exhibiting metal ions in oxidation state +2. On TiO_2(110) in contrast the porphyrin molecules are fully protonated to the diacid form at room temperature, and elevated temperatures are required for metalation. We believe the elevated temperature required for metalation on TiO_2(110) is because titanium is present as Ti^{4+} and therefore has to be inserted into the porphyrin pocket as a titanyl $(Ti{=}O)^{2+}$ unit, which is a more complex reaction.

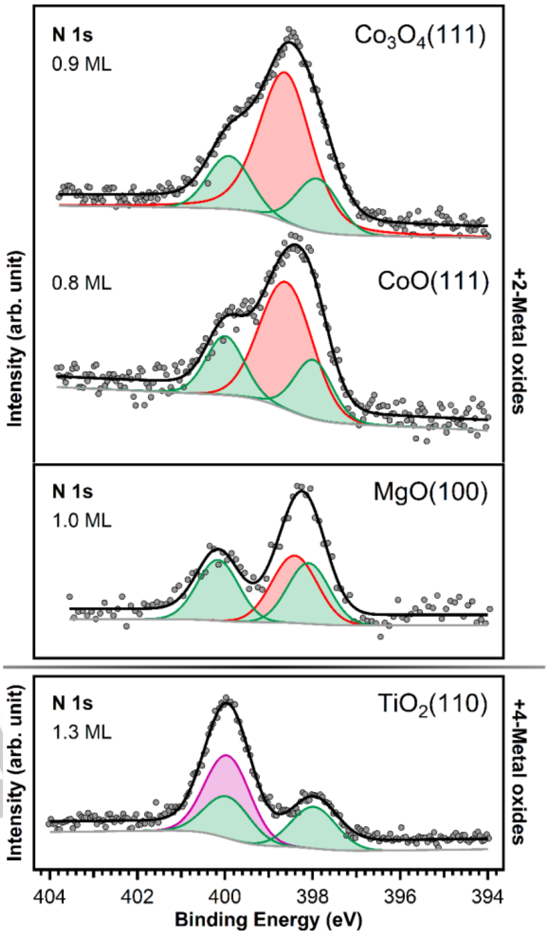

Figure 5. N 1s XPS spectra after adsorption of 2HTPP on Co_3O_4(111) and on CoO(111) at 275 K and on MgO(100)[13] and TiO_2(110)[12] at room temperature.

Experimental Section

X-ray photoelectron spectroscopy measurements were carried out using the Materials Science beamline at the Elettra synchrotron in Trieste, Italy. The end station has a base pressure of 2 × 10^{-10} mbar and is equipped with a SPECS Phoibos 150 hemispherical energy analyzer. Co_3O_4(111) and CoO(111) thin films were grown in situ on a Ir(100) single crystal. The detailed description can be found elsewhere[28]. Briefly, the Ir(100) crystal is cleaned by several sputtering-annealing cycles. Then, it is annealed to 1370 K for 3 min in UHV, exposed to O_2 (10^{-7} mbar, 1270 K) for 5 min and annealed to 1370 K for 1 min in UHV. This resulted in a clean (5×1)-Ir(100) surface, which was oxidized to form a (2×1)−O reconstructed surface by exposure to O_2 (10^{-7} mbar, 1270 K, 5 min) followed by cooling to 370 K in O_2. Cobalt was evaporated onto the (2×1)−O-Ir(100) surface in an O_2 atmosphere (10^{-6} mbar) at 270 K. This is followed by annealing at 520 K for 2 min in O_2 (10^{-6} mbar) and in UHV at 670 K for 10 min creating a Co_3O_4(111) thin film with a characteristic low-energy electron diffraction (LEED) pattern (see Figure 4). The CoO(111) thin films were prepared by annealing the Co_3O_4(111) films to 830 K in UHV resulting in reduction of the film by oxygen loss. The CoO(111) film formed shows its characteristic pattern in LEED (see Figure 4). The thickness of the cobalt oxide films was calculated from the attenuation of the Ir 4f photoelectron signal at a photon energy of 920 eV after correcting for the Co 3p peak (IMFP = 1.39 nm). This resulted in a

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thickness of 7 nm. 2HTPP was purchased from Porphyrin Systems and evaporated using a homebuilt Knudsen cell. We define 1 ML as the coverage that is left on the surface after multilayer desorption at 525 K. This coverage attenuates substrate photoelectrons with a kinetic energy of 100 eV by 50%, and the amount of carbon is in good agreement with previously measured, densely-packed, flat-lying layer of CoTPP on Ag(100) also produced from multilayer desorption[29].

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Keywords: Metalation • Protonation • Ion Exchange • Porphyrins • Oxide Surfaces

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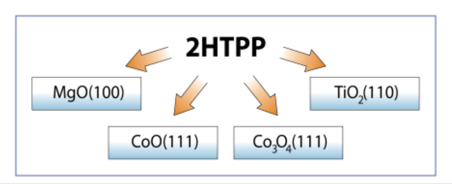

The adsorption and self-metalation of 5,10,15,20-tetraphenylporphyrin (2HTPP) on Co_3O_4(111) and CoO(111) is investigated and compared with previous measurements on MgO(100) and TiO_2(110).

*Author(s), Corresponding Author(s)**

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