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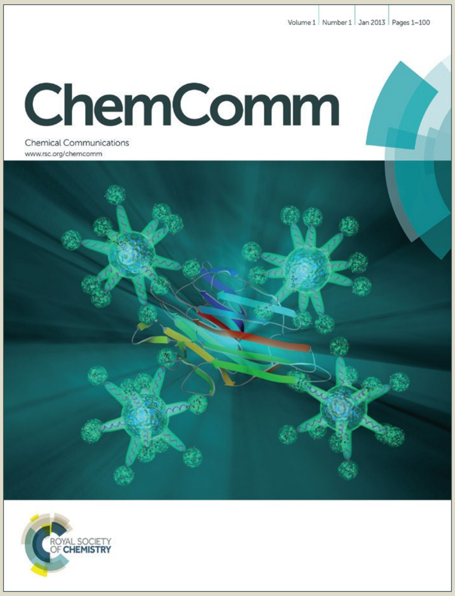

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Immobilised molecular catalysts and the role of the supporting metal substrate

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This work demonstrates that immobilising molecular catalysts on metal substrates can attenuate their reactivity. In particular, the reactivity towards molecular oxygen of both ruthenium tetraphenyl porphyrin (Ru-TPP) and its Ti analogue (Ti-TPP) on Ag(111) was studied as benchmark for the interaction strength of such metal-organic complexes with possible reactants. Here, Ru-TPP proves to be completely unreactive and Ti-TPP strongly reactive towards molecular oxygen; along with comparison to work in the literature, this suggests that studies into immobilised catalysts might find fruition in considering species traditionally seen as too strongly interacting.

One of the current objectives of surface science is to merge the advantages of homogeneous and heterogeneous catalysis,[1] specifically marrying the high regio- and stereo-selectivity found in homogeneous catalysis and the ease of catalytic recovery which is characteristic of heterogeneous catalysis. Recent studies[1a,2] in this field have focussed on immobilising metal-organic complexes, and in particular metallo-porphyrins,[2] onto supporting substrates, aiming to retain their catalytic selectivity but in a heterogeneous environment. In several cases the reactivity of these immobilised metallo-porphyrins, which typically adsorb with their macrocycle parallel to the surface, has been comparatively lacklustre, requiring either low temperatures[2b] or large exposures[2c] in order to coordinate adducts to the metal centre of the metallo-porphyrin. Nevertheless, as will be demonstrated below, the reactivity for species containing strongly interacting metal centres is not completely quenched. This suggests that the interaction with the supporting surface, acting as a pseudo-2D-ligand,[2d,e] is detrimental to the catalytic activity of such immobilized species, shifting the so-called “Volcano plot” of the Sabatier principle[3] towards more reactive metal centres.

In general the Sabatier principle describes the “Goldilock’s zone” for catalytic activity, where the interaction between the catalyst and the adsorbed reactant species is strong enough to drive a reaction forward, but not so strong that the active sites of the catalyst become blocked by tightly bound reaction intermediates. If, for example, catalysts are too weakly interacting with the reactants, the period of time that the latter are bound to the active site may become comparable to (or even smaller than) the period of time it takes for the reaction to proceed. In this case, the catalytic activity becomes time-dependent and diffusion limited.[3a] Conversely, if the catalyst is too strongly interacting with the adsorbed reactants then reaction intermediates may be stabilised at the active site resulting in a smaller energy difference between the released final product and the adsorbed intermediate species, such that the forward action of the catalytic reaction becomes thermodynamically less favourable. In this case, the catalytic activity becomes energy dependent.[3a] Therefore, plotting catalytic activity as a function of interaction strength (e.g. heat of adsorption)[3b] results in the aforementioned “Volcano plot”. Such Volcano plots are ubiquitous within catalysed reactions (with the exception of radical mediated polymerisation)[3a] and often have platinum group metals (e.g. ruthenium) near the peak of the “volcano”, and group XI (e.g. silver) and group IV metals (e.g. titanium) at the base of the “volcano” due to, respectively, interacting too weakly, and too strongly with reactants. Here we present a comparison between the activity towards molecular oxygen of ruthenium tetraphenyl porphyrin (Ru-TPP – shown schematically in Fig. 1) and titanium tetraphenyl porphyrin (Ti-TPP) adsorbed onto a Ag(111) surface.† In liquid phase experiments, Ru-porphyrins have excellent catalytic activity for alkene/olefin epoxidations,[4] where the metal centre switches between an oxo- and a dioxo- species, with the dioxo species being the catalytically active. More broadly,

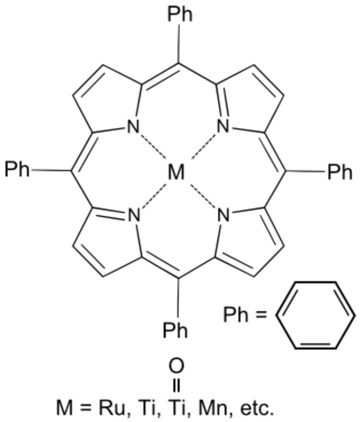

Fig 1. Molecular schematic of a metallo-tetraphenyl porphyrin (M-TPP), where M, the metal centre, can take a variety of forms, eg. Ru for Ru-TPP, Ti for Ti-TPP, TiO for TiO-TPP and Mn for Mn-TPP.

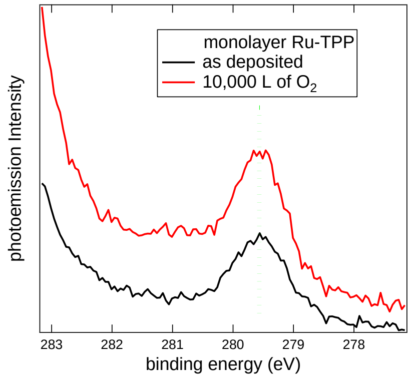

Fig. 2 Ru 3d$_{5/2}$ XP spectra before (black, lower line) and after (red, upper line) exposure to 10,000 L of O$_2$.† The dashed green line indicates the centre of the peak. If a chemical change was present after oxygen exposure, a shift in binding energy should be observed e.g. ref 9.

Ru-porphyrins - like Ru-TPP - have been observed to cleave molecular oxygen, forming either a di-oxo[4a] or a dimer system.[5] The formation of an oxo-species is regarded as a necessary intermediate step in an epoxidation reaction and, specifically, the interaction of the metal centre with molecular oxygen may be utilised as a broad measure for the interaction strength of such catalysts. However, when adsorbed on a Ag(111) surface, the Ru-TPP is observed, via the chemical sensitivity of X-ray photoemission spectroscopy (XPS), to be completely unreactive towards molecular oxygen and, even upon comparatively large exposures (10,000 Langmuirs (L) – Fig. 2), no oxo-ruthenium species can be identified. For comparison, the dissociative sticking probability of oxygen on Ag(111) has been found to be 10^{-5}-10^{-6} (e.g. ref 6) and, disregarding the Ru-TPP, one would expect around 0.5-5 adsorbed oxygen atoms per 100 silver atoms after an exposure of 10,000 L, a coverage which should be sufficient to oxidise between 14 and 100% of the Ru atoms,†† assuming a process similar to that found by Sedona et al. in the oxidation of iron phthalocyanine on Ag(110).[7] This implies that, compared to the aforementioned Ru-porphyrins in liquid phase, not only does the Ag surface passivate the active site of the Ru-TPP molecule, but also it seems that the Ru-TPP itself passivates the Ag surface. The former can likely be attributed to a strong interaction between the metal centre and the substrate, which is supported by the binding energy of the corresponding Ru 3d$_{5/2}$ feature, which more closely resembles a Ru(0) state rather than the Ru(II) state of isolated Ru-TPP.[8] To further test this apparent "surface-induced" quenched reactivity of Ru-TPP, the molecular layer was also exposed to 4,000 L of N$_2$O and 500 L of CO. The former has been employed as an alternate route to oxidise Ru-porphyrin species;[10] the latter species is commonly used as a protecting ligand for Ru-TPP under ambient conditions. In both cases the Ru 3d$_{5/2}$ spectra show no chemical modification, again suggesting that the reactivity of the Ru-TPP on Ag(111) has been attenuated (see Fig. SI 3).

In contrast, upon a relatively small exposure to molecular oxygen (~75 L), near complete oxidation of Ti-TPP to oxo-titanium tetraphenyl porphyrin (TiO-TPP) is observed (Fig. 3). Oxidation results in a binding energy shift in the main peak of the Ti 2p$_{3/2}$ spectrum from 455.8 eV for Ti-TPP (Fig. 3e) to 457.8 eV for TiO-TPP (Fig. 3b), and a significant decrease in the apparent height of the molecule in STM (Figs. 3d and 3a, respectively). Specifically, after an exposure of only ~15 L, the oxidation of the centrally coordinated Ti centre is already observed to have begun with the binding energy region between 457 and 458.5 eV in the Ti 2p$_{3/2}$ XPS, which corresponds to the TiO species, dramatically increasing in intensity (changing rapidly from red to purple to dark yellow in Fig. 3c). Furthermore, after an exposure of ~40 L, there is a notable decrease of intensity in the binding energy region between 455 and 456 eV that corresponds to Ti-TPP (changing from red to cyan/blue in Fig. 3c). Finally after an exposure of ~75 L the TiO species seems to have effectively saturated in intensity (gradual change from dark to light yellow in Fig. 3c), which would correspond to a dissociative sticking coefficient of the Ti atoms of ~10^{-1}.†† Note that the intensity of the peak that corresponds to TiO-TPP is notably higher than the main peak (Ti-a) of the Ti-TPP species, resulting in a significant overlap of the two species in Fig. 3c. This is due to a significant higher binding energy feature in the Ti-TPP spectra (labelled Ti-b), which will be discussed further in a future publication,[13] however it is not thought to arise from multiple chemical different species on the surface, as indicated by only one Ti-TPP species being observed in the STM measurements (see Fig. SI 4 in the supporting information). The binding energies of the main peaks in Ti 2p XPS for Ti-TPP and TiO-TPP correspond well with those of the expected oxidation states of complexed Ti centre, specifically 2+ for Ti-TPP and 4+ for TiO-TPP. Additionally a shift in binding energy is observed between Ti evaporated on the Ag(111) surface and the Ti-TPP species, and between oxidised Ti on Ag(111) (TiO$_x$) and TiO-TPP (Fig. 4 – binding energies listed in table SI 1).

However, as alluded to above, it is not sufficient for a catalyst to interact strongly enough to begin a reaction, it must also form an intermediate species that is bound weakly enough such that the next step of the reaction can proceed. In the case of TiO-TPP, annealing the Ag(111)/TiO-TPP system to 750 K at 0.5 K/s revealed a remarkably stable TiO moiety. As shown in Fig. 5, apart from a slight decrease in intensity due to some minor desorption of the entire TiO-TPP molecule (which is attributed to a cyclodehydrogenation reaction between the macrocycle and phenyl rings, described elsewhere)[11] no chemical changes in the remaining Ti 2p spectra are observed. Thus, inferred from its thermal stability, the Ti-O bond is likely too strong for TiO-TPP on Ag(111) being utilised as the oxidant in reactions such

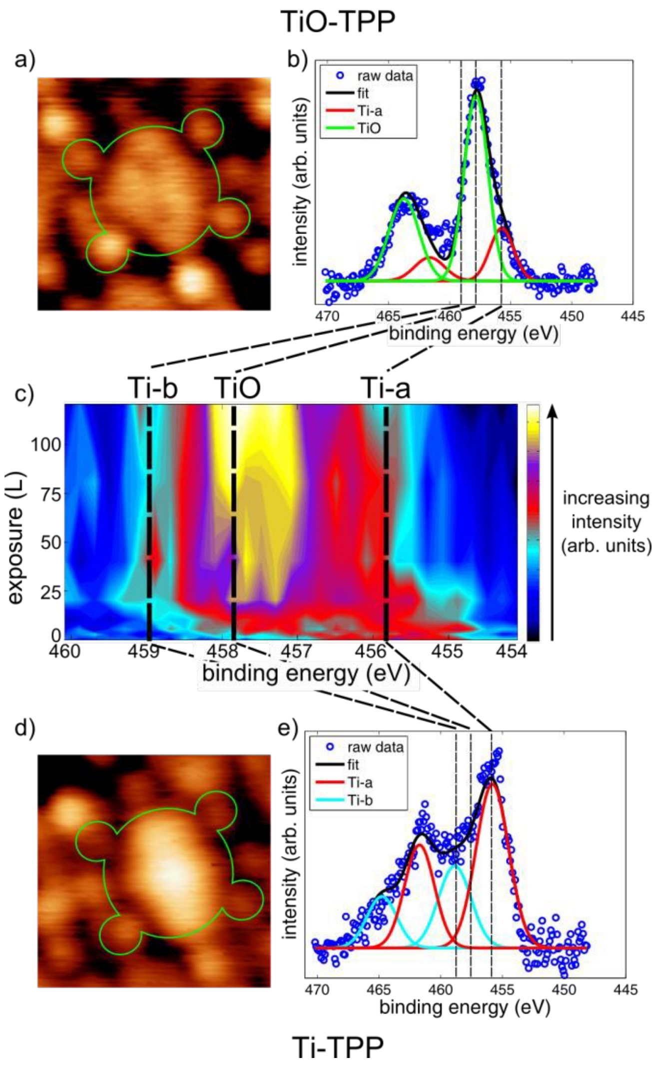

Fig. 3 STM images (2.3×2.3 nm^2, 0.3 V, 0.12 nA) and Ti 2p XP spectra for both (a,b) TiO-TPP, and (d,e) Ti-TPP species. Also shown are (c) Ti 2p$_{3/2}$ XP spectra as a function of oxygen exposure.† Green shapes in the STM images indicate the expected outline of the molecule, based on a free-base tetraphenyl porphyrin species adsorbed on the same surface. Dashed-black lines indicate the centre of the Ti-a, Ti-b and TiO species for the XP spectra.

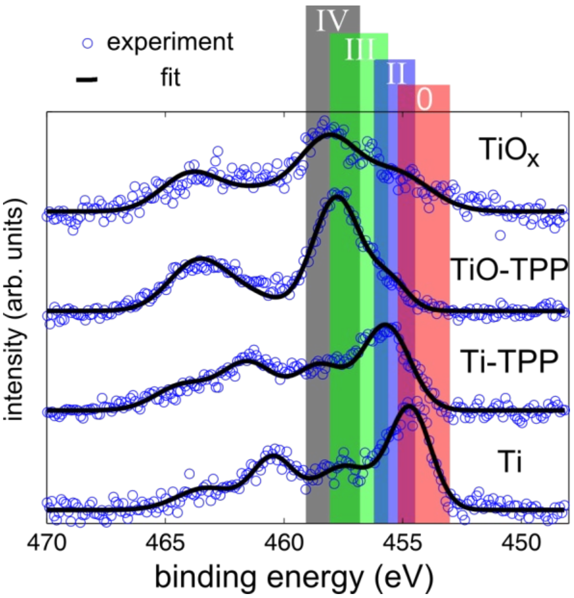

Fig. 4 Ti 2p XP spectra of titanium evaporated onto Ag(111) before (Ti) and after (TiO$_x$) oxidation without any TPP present, compared against the same spectra for Ti-TPP and TiO-TPP. Overlaid are the binding energies for various Ti states found in the literature.[14]

as epoxidation (though the Ti-O moiety may be catalytically active itself).[12]

In summary, immobilising Ru-TPP onto a Ag(111) surface apparently quenches its reactivity, whereas its Ti analogue, Ti-TPP, readily forms a strongly bound oxo-species upon a comparatively low exposure of molecular oxygen. It is important to note that overlayers of both species have similar packing on the substrate,11,13 such that, broadly, the only difference between the two layers is the presence of Ti atoms instead of Ru atoms at the centre of the molecules. To the authors' knowledge, there is only one other study present in the literature that has attempted to create an oxo-metal porphyrin species on the surface of Ag(111), notably the work of Murphy et al.2b with Mn-TPP on Ag(111). Manganese is typically observed to interact more strongly than ruthenium, but significantly more weakly than titanium. Keeping this in mind, what Murphy et al. observed was that the Mn metal centre - in contrast to Ru and Ti - reversibly reacted with molecular oxygen. After an exposure of 10,000 L, the surface was saturated with MnO-TPP (implying a sticking coefficient of ~10-3†† to the Mn atoms), which could then be reduced to Mn-TPP by annealing to ~425 K. Importantly, the ability of the Mn-TPP on Ag(111) to reversibly interact with molecular oxygen implies that it could well catalyse an epoxidation reaction (as opposed to Ti-TPP and Ru-TPP that would likely have a reaction rate of effectively zero), however the low sticking coefficient could also imply that its catalytic activity will be time dependent – i.e. that it would exist on the "too weakly" interacting slope of the volcano plot from the Sabatier principle. This suggests that the ideal metal centre for such a metallo-porphyrin species immobilised on a metal surface may well be found amongst elements that are traditionally thought of as too strongly interacting for homogeneous catalysis (e.g. Cr, Ta, V, Nb, etc.). Furthermore, the apparent "surface- induced" quenching of reactivity implies that the influence of the supporting substrate on the centrally coordinated metal may have comparable influence on the reactivity of these species as the other ligands coordinated to it (in the case of TPP, its

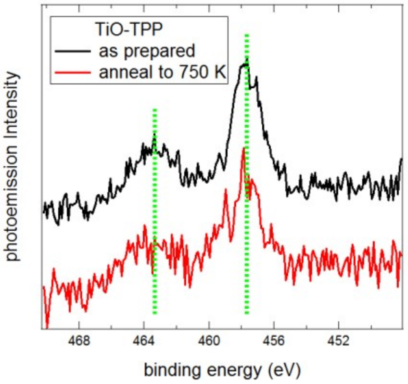

Fig. 5 Ti 2p XP spectra before / after annealing a monolayer of TiO-TPP to 750 K.† The dashed green lines indicate the centre of the spin-orbit split Ti 2p features.

four conjugated pyrrole groups), similar to the effect that has been recently coined the “surface-trans effect”.[2d] The origin of this quenching has not yet been fully elucidated, however there does appear to be some charge transfer from the substrate into the unoccupied states of the metal centre (e.g. refs. 15), resulting in the metal ion occupying an oxidation state that can be significantly different from the isolated molecule (as mentioned above with the Ru in an apparent (0) instead of (II) state), but with the available data it is not clear if this charge transfer is the cause of the quenched reactivity, originates from the same cause, or if it is even related. That the Ti atoms in Ti-TPP occupy an apparent (II) state, on the other hand, does substantiate the idea that a surface-altered oxidation state is the origin of the quenched reactivity of the complexed Ru centre.

Finally, a major requirement for the application of such novel heterogeneous systems, inspired by homogenous ones, is that the immobilised species must have a comparatively strong interaction with the substrate, specifically a stronger interaction than it has with a potential solvent (to prevent the catalyst dissolving into the solvent). This would mean that either the metal-organic species should be immobilised by a functional group that is distant to the active site, or, as already outlined, that the substrate itself becomes a parameter to optimise when designing the catalyst.

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Notes and references

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† See experimental details in ESI

†† See sticking coefficient calculation details in ESI

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