Interfacial Chemistry and Catalysis of Inorganic Materials

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Abstract: Heterogeneous catalysis is essential to most industrial chemical processes. To achieve a better sustainability of these processes we need highly efficient and highly selective catalysts that are based on earth-abundant materials rather than the more conventional noble metals. Here, we discuss the potential of inorganic materials as catalysts for chemical transformations focusing in particular on the promising transition metal phosphides and sulfides. We describe our recent and current efforts to understand the interfacial chemistry of these materials that governs catalysis, and to tune catalytic reactivity by controlled chemical modification of the material surfaces and by use of interfacial electric fields.

Keywords: Chemical surface modification · Heterogeneous catalysis · Interfacial electric field · Surface chemistry · Transition metal phosphides · Transition metal sulfides

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1. Introduction

Most chemicals in the chemical industry are produced using a heterogeneous catalyst, which is a solid material that changes the rate of a reaction without being consumed.[1] Many current processes employ noble-metal based catalysts, which typically exhibit superior catalytic performances. However, noble metals are rare and expensive and thereby pose one major limitation in the development of sustainable chemical processes. Furthermore, metal catalysts can be susceptible to poisoning and often do not produce the desired product with sufficient selectivity. For example, the typical heterogeneous Pt- or Pd-based catalysts for industrial hydrogenation reactions usually form alkanes as major products from the corresponding alkynes and H_2, and saturated aldehydes from α,β-unsaturated aldehydes and H_2 rather than the products that would be particularly desirable, *i.e.* alkenes from alkynes or allylic alcohols from α,β-unsaturated aldehydes.[2,3] While some selectivity enhancement can be achieved by size control of nanoscale metal catalysts, or by admixture of a second element such as tin,[2–4] selectivity remains a major challenge in current heterogeneous catalytic processes. More sustainable chemical processes would be obtained by developing earth-abundant materials as catalysts that show high activity for chemical transformations similar to noble metals but with higher selectivity and higher stability.

Transition metal phosphides (TMP) and transition metal sulfides (TMS) have shown promising catalytic properties in some applications and the potential to complement or perhaps even replace noble-metal based catalysts.[5–8] However, this potential is currently not exploited much. The development of TMP and TMS in catalytic applications is hampered by a lack of understanding of the chemistry happening at the solid-fluid interface that governs catalysis. Because the interfacial chemistry of TMP and TMS is not well understood, efforts to tune these materials for a specific application are currently largely restricted to empirical approaches. To address these challenges the Delley group explores TMP and TMS for both thermal and electrocatalysis. We are targeting a fundamental understanding of the operative interfacial chemistry in the catalysis by TMP and TMS materials and the development of effective approaches for a controlled tuning of their catalytic properties. Combined, this could provide new opportunities to expand the catalytic universe of TMP and TMS materials. Herein, we provide a perspective on the state of the art of transition metal phosphides and sulfides in catalysis and outline our research efforts in this area (Fig. 1).

2. Transition Metal Phosphides and Transition Metal Sulfides in Heterogeneous Catalysis

TMP and TMS exist in a variety of M_xP_y and M_xS_y x:y compositions that show a range of structural and electronic properties.[9,10] This compositional flexibility also results in a range of catalytic properties, which offers great opportunities to select a material according to the requirements of a particular chemical transformation. For instance, the metal-rich TMP and TMS (*i.e.*, compositions with x≥y) have metallic character that imparts good

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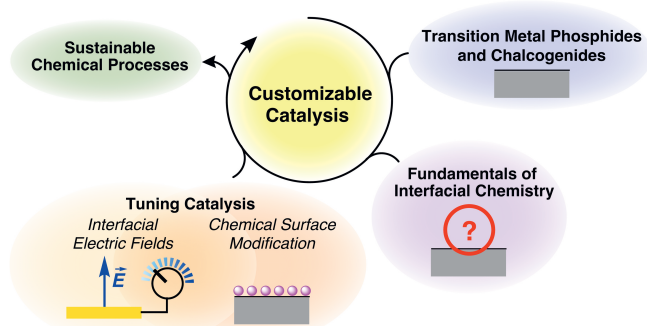
Fig. 1. Overview over the research directions being pursued in the Delley group.

electrical conductivity to the materials. This makes metal-rich TMP and TMS suitable for electrocatalysis. For instance, TMP and TMS have shown promise as electrocatalysts for water splitting: for both the electrocatalytic hydrogen evolution reaction (HER)[5,6] and the oxygen evolution reaction (OER).[11–13] One advantage of TMP for HER applications comes from their enhanced corrosion resistance compared to the pure metals due to the presence of P.[5] Under the oxidative conditions of OER, TMP and TMS present oxidized $M_xO_y(OH)_z$ surfaces that are thought to be catalytically active.[14] Interestingly, surface-oxidized TMP and TMS have been shown to outperform directly prepared $M_xO_y(OH)_z$ materials.[13–19] The origin of the superior performance of surface-oxidized TMP and TMS over $M_xO_y(OH)_z$ materials for OER has been variously attributed to enhanced conductivities, larger surface areas, an easier formation of high-valent metal sites, or to chemical effects from the presence of P- or S-based species.[14,17,20–22] In our group we are examining the basic chemistry behind the ability of TMS and TMP to catalyze HER and OER in order to develop these materials in new catalytic applications.

In addition to the electrocatalysis of water splitting, TMP and TMS have previously also shown excellent catalytic properties for thermal catalysis, in particular for hydrotreating applications.[7,10] In hydrotreating, elemental contaminants, such as S, O, and N, are removed from organic substrates in fuel feeds by reaction with H_2. Today, commercial hydrodesulfurization catalysts are based on TMS.[23] More recently, the exceptional properties of TMP for hydrotreating catalysis have been discovered. These materials have not only shown high activity but also improved stability against sulfur-poisoning compared to more conventional metal catalysts.[24,25] TMP are hence currently being discussed as potential future alternatives for hydrotreating applications.[7,26]

The ability to efficiently activate H_2 is one key factor that makes TMP and TMS superior catalysts for hydrotreating. This ability is also critical to the hydrogenation of multiple bonds. TMP and TMS have indeed been shown to be highly efficient catalysts for the hydrogenation of alkenes, alkynes, nitriles, nitro-groups, and carbonyl groups.[10,27–35] In these reactions TMP and TMS materials not only exhibited high catalytic activity and stability, but also interesting catalytic selectivity. For instance, cobalt phosphide (CoP) and nickel phosphides (Ni_xP_y) catalyze the hydrogenation of alkynes with preferential formation of the semihydrogenated product, the alkene, which is of interest for the synthesis of pharmaceuticals and other chemical products.[30–33] In the hydrogenation of α,β-unsaturated aldehydes, TMP materials also exhibit interesting chemoselectivities that are distinct for compositionally different TMPs. This showcases the versatility of this class of materials as catalysts. Some TMP preferentially hydrogenate the C=C group, some the C=O group, and others give predominantly the fully hydrogenated product. For instance, Ni_xP_y has been shown to selectively hydrogenate cinnamaldehyde (CAL) to

the corresponding saturated aldehyde (hydrocinnamaldehyde, HCAL), while iron phosphide (Fe_2P) preferentially formed the saturated alcohol (hydrocinnamalcohol, HCOL) under similar conditions.[34] Our group has recently reported that CoP hydrogenates CAL with initial formation of roughly 50% COL and 50% HCAL.[35] Because allylic alcohols such as COL are the thermodynamically more challenging products to form, this shows that CoP has a kinetic preference for C=O hydrogenation. These catalytic properties are of particular interest, because allylic alcohols are valuable intermediates in the production of pharmaceuticals, fragrances, and flavors. The predominant formation of an allylic alcohol from the hydrogenation of α,β-unsaturated aldehydes cannot typically be achieved using pure noble metal-based catalysts. Noble metals preferentially hydrogenate C=C over C=O bonds and usually produce the allylic alcohol in minor amounts only.[2,3] In case of CoP the initial catalytic selectivity is quite promising, but secondary reaction pathways limit the production of the desired allylic alcohol.[35] We have shown that the COL formed with CoP further reacted to allylbenzene (AB) and β-methylstyrene (MS), likely *via* hydrogenolysis of the C–O bond and *via* deyhdration, respectively (Scheme 1).[35] Therefore, the catalytic selectivity of CoP needs to be further tuned in order to improve the catalytic performance. Potential strategies for such a tuning are further discussed in section 4.
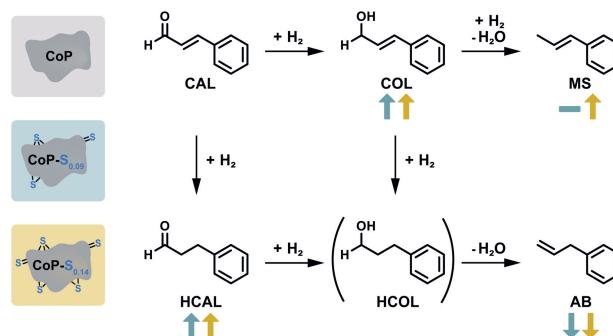
Scheme 1. Possible reaction pathways for the hydrogenation of cinnamaldehyde using CoP. The arrows under each reaction product show enhanced, decreased, or unchanged productivity obtained with S-modified CoP having an intermediate (CoP-$S_{0.09}$) or a large S content (CoP-$S_{0.14}$) compared to the bare CoP. Scheme adapted from *J. Am. Chem. Soc.* **2023**, *145*, 23556.

Overall, the chemical transformations that are catalyzed by TMP and TMS exemplify the potential of these materials for both thermal and electrocatalysis. Our results show that TMP and TMS can exhibit alternative as well as similar selectivity as noble metals while still showing high activity. This offers new opportunities for the implementation of these earth-abundant materials in catalytic applications. Critical to realizing the full potential of TMP and TMS in catalysis is a fundamental understanding of the surface chemistry that directs their catalytic reactivity.

3. Fundamentals at the Surface

The HER and hydrotreating catalysis by TMS and TMP imply that these materials allow the intermediate binding of hydrogen at the surface. Density functional theory (DFT) studies suggest that P-sites actively participate in H-binding as proton acceptors, while metal sites act as hydride acceptors.[36] Delley *et al.* have shown that TMPs have a high capacity for hydrogen chemisorption on the order of one H per surface metal atom.[30] Furthermore, hydrogen was shown to occupy different types of sites with a range of binding energies.[30] According to the Sabatier principle, the best heterogeneous catalysts exhibit an intermediately

strong binding of reaction intermediates at the surface.[37–38] With a binding that is neither too weak nor too strong, reactants can be activated at the surface and products can desorb allowing catalytic turnover. Theoretical studies suggest that P- and metal atoms in TMP lead to favorable binding energies of H in a synergetic way.[36] It has further been shown that incoporation of a small amount of sulfur into TMP catalysts can enhance the catalytic activity of the materials for both HER and hydrotreating applications.[39–44] This S-effect has usually been attributed to an optimization of the H-binding energies to the surface that is key to both reactions.[40,41,45,46] However, conventional methods of catalyst preparation lead to sulfur incoporation both in the bulk and at the surface of TMP materials, which hampers the derivation of clear structure-reactivity relationships.

We have recently developed an approach that allows the controlled delivery of sulfur-dopants to the surface of TMP materials.[35] Reaction of CoP with a series of molecular S-transfer reagents, namely different phosphine sulfides (SPR_3), transferred sulfur to CoP (Fig. 2a). Because the SPR_3 cannot move into the bulk of the material, the S-delivery is to the CoP surface only. Our results showed that the number of S atoms transferred to CoP after equilibration of the reaction depended on a specific SPR_3 reagent used and correlated with the corresponding P=S bond strength of the SPR_3 reagent. These observations showed that reactions with different SPR_3 populate different types of S-sites at the surface of CoP. The notion that there is not just one single type but *a distribution of different sulfur sites* on the CoP surface is in line with the amorphous nature of the heterogeneous CoP surface, for which multiple different sites are expected.

Secondly, our approach involving chemical equilibration of CoP with molecular S-transfer reagents also provided quantitative measures of the binding strengths of S to the CoP surface (Fig. 2b).[35] This is because an S-transfer can only occur if stronger bonds are formed on the CoP surface than present in the SPR_3 reagent (assuming other contributors to the reaction free energy can be neglected). We can thereby derive binding strengths of

S to CoP that are in the range of 69-84 kcal/mol bracketed by the different SPR_3 reagents used. Our work therefore provides important information about how sulfur binds to a complex, amorphous TMP surface that is typical[30,47,48] for heterogeneous catalysts. S-binding energies have previously been correlated with catalytic activity in hydrodesulfurization using so-called Volcano plots.[49–51] The S-binding energies in these plots have been calculated from bulk properties of sulfide materials and hence, one single M–S bond energy is derived as a descriptor of catalytic activity for each material. However, our work suggests that the presence of a distribution of S-sites having a range of binding strengths needs to be taken into account in order to provide a more realistic picture of catalytic TMP surfaces.[35] We propose that the S-bond strengths we derived for the amorphous CoP surface could be used to probe the predictive nature of Volcano plot considerations in the hydrotreating catalysis by CoP and similar TMPs.

This work exemplifies on-going efforts in our group to obtain insight into the fundamental surface properties that govern catalysis. For this, we combine methods of molecular chemistry with a range of spectroscopy and microscopy for material characterization.

4. Strategies to Tune Catalytic Properties

Above, we outlined the promising catalytic properties of TMP and TMS. However, actual implementation of these materials in industrial processes often requires further enhancement of their catalytic activity and selectivity. Heterogeneous catalysis operates *via* the surface of a catalytic material and is governed by inner-sphere interactions at the solid-fluid interface that result in bond breaking and bond making processes. Catalytic properties could hence be tuned by directing this interfacial chemistry in a controlled manner. This may be achieved using similar strategies as in the fields of molecular and enzymatic catalysis, which involves the careful design of active site structures and their environment.[52] In the Delley group we pursue the electronic and steric control of catalytic surfaces through methods of chemical surface modification and through the use of interfacial electric fields.

4.1 *Chemical Surface Modification*

Chemical modification of surfaces can induce electronic and/or steric control over catalysis and hence take a similar role in heterogeneous catalysis as the design of ligands for organometallic complexes in homogeneous catalysis. TMP and TMS surfaces have previously been modified with organic groups, which have been shown to enhance electrocatalytic HER activity of these materials. For instance, Miller and coworkers have functionalized MoS_2 HER catalysts with differently substituted phenyl groups and showed that the most electron-donating substituent led to the most efficient HER catalyst in the series and a more stable performance than the bare MoS_2.[53] A similar functionalization approach has successfully been implemented by Cossairt and coworkers to enhance HER activity and stability of nickel phosphide nanoparticles.[54] Brutchey and coworkers have shown that carbene-ligands for copper phosphide nanocrystals enhanced their HER activity when compared to the as-prepared oleylamine-ligated particles.[55] These studies exemplify the great potential of surface modification approaches for the tuning of catalysis by TMP and TMS. However, organic surface groups can also inhibit catalysis by poisoning active sites or by blocking access of substrates to the surface.[56] This effect can be minimized by modifying TMP and TMS surfaces with individual atoms rather than large organic ligands.

Atom-doping has indeed emerged as a very successful strategy to enhance the catalytic properties of TMP and TMS.[57–60] Various metal- and main-group atom dopants have been shown to enhance catalytic activity. For instance, sulfur-modified TMP has shown a higher catalytic activity for electrocatalytic HER than the
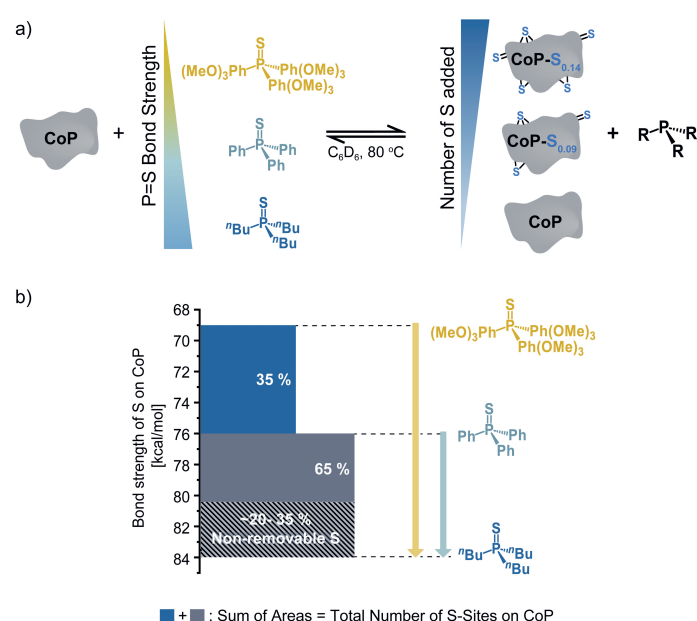

Fig. 2. a) Equilibration of CoP with different SPR_3 added different amounts of sulfur to the CoP surface according to the P=S bond strength of the corresponding SPR_3 reagent with R = *n*Bu, Ph, or Ph(OMe)$_3$ (= tris(2,4,6-trimethoxyphenyl)) b) Bond strength distribution for sulfur binding on CoP derived from chemical equilibration studies. The data show that there are multiple different types of S-sites on the surface that have different bond strengths. Figure adapted from *J. Am. Chem. Soc.* **2023**, *145*, 23556.

pure TMP or TMS materials.[39,40,46,61] It is interesting that a very similar effect of sulfur on the catalysis by TMP materials has also been observed for thermal hydrotreating, in which the formation of metal phosphosulfides on the surface of TMPs under reaction conditions are thought to promote catalysis.[44,62–64] Our approach to transfer sulfur to the surface of TMP materials using molecular S-transfer reagents described in the previous section not only offered a controlled method to modify the surface of CoP but also enables the introduction of a specific number and type of sulfur (Fig. 2).[35] We thus prepared a series of CoP materials containing a different number and type of sulfur at the surface and tested these as catalysts for the hydrogenation of cinnamaldehyde (CAL). Our results revealed that sulfur on the TMP surface influenced the catalytic properties by acting in a dual role as both promoter and poison of catalysis. The extent of these effects depended on the number and the binding strength of S on CoP (Scheme 1). As a poison, sulfur minimized a secondary reaction pathway: the dehydration of cinnamalcohol (COL) to allylbenzene (AB), which lead to a desired enhancement of the selectivity for COL. As a promoter, sulfur on CoP also improved the productivity of the hydrogenation products HCAL and COL. However, sulfur also had undesired effects on hydrogenation catalysis: especially large amounts of sulfur on CoP decreased the material's initial activity and accelerated another secondary reaction pathway from COL to β-methylstyrene (MS) leading to a decreased selectivity for hydrogenation products. Overall, our results show that sulfur on CoP has both desired and undesired effects on hydrogenation catalysis. With some but not too much sulfur on the CoP surface and with sulfur that is bound with intermediate bond strengths to the material surface an optimal balance of catalytic properties can be achieved for the hydrogenation of cinnamaldehyde. Hence, *a precise control over both the number and the type of exposed surface dopants is needed for the design of CoP catalysts*. It is likely that similar considerations apply to other TMP catalysts.

4.2 *Interfacial Electric Fields*

Electric fields are known to impact catalytic reactions. Indeed, substantial electric-field effects on chemical reactions have been theoretically predicted.[65] Such effects can also be found in nature. The enormous power of enzymes for catalysis has been attributed to electrostatic preorganization.[66–68] The specific positioning of charged and polar residues has been suggested to generate electric fields that are key to drive the high reactivity of biological catalysis in enzymes. Extending this principle, molecular systems equipped with charged functionalities generate an internal directional electric field, which has been shown to enhance the selectivity in the molecular (electro-)catalysis of *e.g.* CO_2 or oxygen reduction reactions.[69–71] Similarly, electric fields at the solid-fluid interface can be harnessed in electrocatalytic applications or in thermal heterogeneous catalysis.[72,73] High-profile examples include experimental studies on epoxide rearrangements, hydrogenations, Brønsted acid catalysis, and anion-π catalysis that show considerable electric field effects on catalytic activity or selectivity.[74–78]

Interfacial electric fields can be generated by applying an electrochemical potential to an electrode. We have recently shown that this can generate very large electric fields at the surface in the order of 10^9 V/m.[79] In this work we tested the effect of the electric field on the acidity of a mixed self-assembled monolayer (SAM) on gold that contained both carboxylic acid and nitrile functionalities (Fig. 3a). The applied electric fields modified the effective pK_a values of the carboxylic acids of the mixed SAM by 1-2 units. This corresponds to a change of free energy of 1.4-2.7 kcal/mol demonstrating that both thermochemistry and reactivity at a solid/solution interface can be significantly influenced. Electric fields hence emerge as a promising agent at the interface to control chemical properties and reactions.
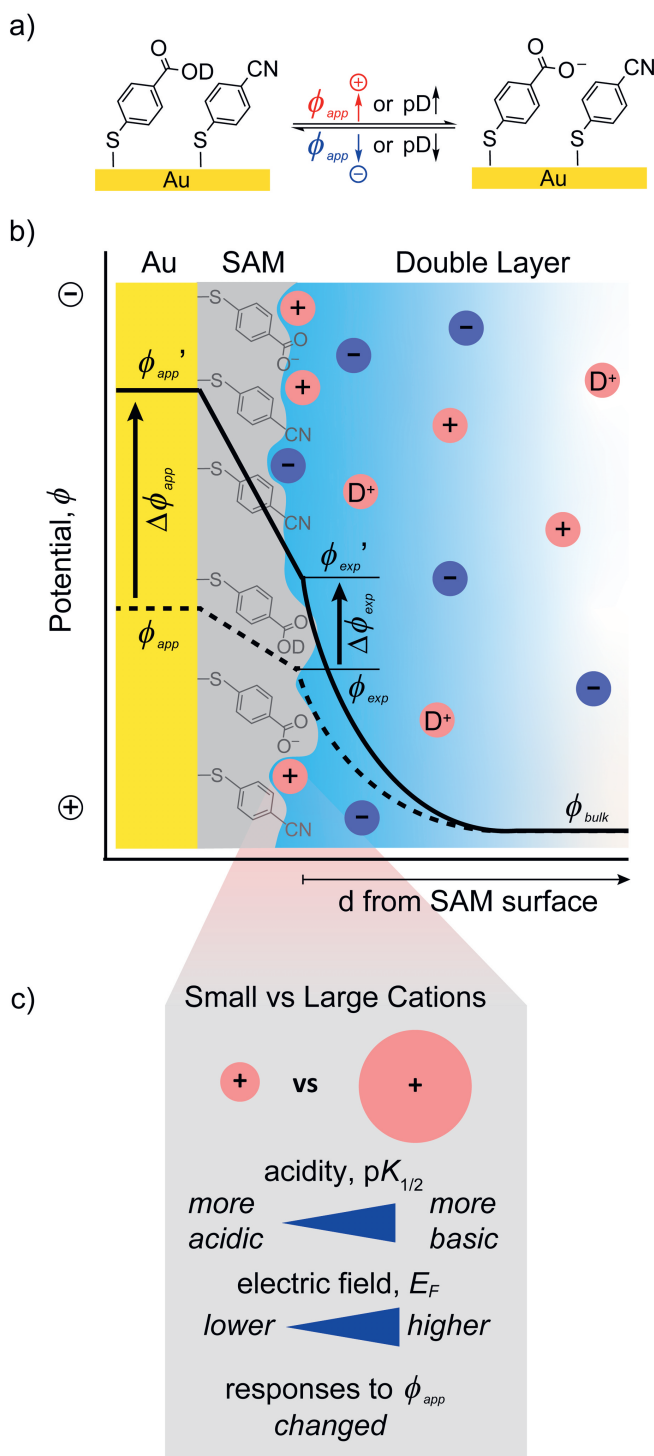
Fig. 3. a) Acid/base equilibria at the interface of a mixed self-assembled monolayer (SAM) supported on gold containing mercaptobenzoic acid as an acidic component and mercaptobenzonitrile as a Vibrational Stark probe of the interfacial electric field. The applied potential ϕ_{app} generates an interfacial electric field that shifts the acid/base equilibrium and modifies the effective pK_a value of the monolayer. b) Potential drop at the solid/fluid interface of the mixed SAM on gold. The experienced change in potential $\Delta\phi_{exp}$ is much smaller than the $\Delta\phi_{app}$ applied. c) Varying the size (and nature) of electrolyte cations has large effects on acidity, electric field, and their changes with ϕ_{app}. Figs. 3 a,b are reprinted with permission from *J. Am. Chem. Soc.* **2021**, *143*, 10778. Copyright 2021 American Chemical Society. Fig. 3c is adapted with permission from *J. Phys. Chem. C* **2022**, *126*, 8477. Copyright 2022 American Chemical Society.

However, interfacial electric field effects are convoluted with a range of complex phenomena at the interface. For instance, recent work has emphasized the difference between electric field effects

and through-bond electro-inductive effects.[80–83] Using surface-enhanced infrared absorption spectroscopy (SEIRAS)[84] and the Vibrational Stark effect[85] we were able to directly measure the electric field that is actually experienced at the surface as a function of the applied potential using the nitrile functionalities of a mixed SAM (Fig. 3).[79] We have shown that the experienced field is only a fraction of the field that is experimentally applied to the electrode, but it is this experienced field that determines surface reactivity (Fig. 3b).[79] The interfacial electric field is also largely influenced by other interfacial components and this in turn impacts surface properties. For instance, variation of the electrolyte cation identity and the applied electrochemical potential combined can change acid/base equilibria at the surface by 3 orders of magnitude (Fig. 3c).[86] Further study is critically needed to understand the complex interplay between the interfacial electric field and the chemistry happening at the solid-fluid interface. In the Delley group we use spectro-electrochemical approaches to elucidate the effect of electric fields on the interfacial chemistry and catalysis of inorganic materials.

5. Conclusions

Transition metal phosphides and transition metal sulfides have shown promise as heterogenous catalysts for some applications with similarly high activity and sometimes alternative selectivity as noble metals. In our group, we aim to build on this potential by tuning the catalytic selectivity and activity of these inorganic materials through controlled surface modification strategies. Our work on sulfur-dopants at the surface of TMP materials has shown that both the number and type of surface sites that are occupied by sulfur dopants can diversely affect catalytic performance. This highlights that the presence of a distribution of surface sites needs to be considered in order to develop effective strategies to enhance the catalytic performance of complex materials.

In addition to the strategies that are based on chemical modification of surfaces to tune heterogeneous catalysis, electric fields can provide a powerful control element over catalytic properties. We have shown that externally applied electric fields can have very large effects on surface properties and surface reactivity of self-assembled organic monolayers on gold. Spectro-electrochemical approaches revealed that the experienced field is distinct from what is applied. This work also exemplified the large influence of solution components on interfacial electric field effects. These findings present important steps in understanding how electric fields could be implemented as a control element in interfacial chemistry and catalysis.

In the Delley group we are exploring earth-abundant inorganic materials in heterogeneous catalysis. We target further development of these promising materials for the catalysis of chemical transformations through fundamental insight on their interfacial chemistry that governs catalysis. By harnessing the power of controlled surface modification strategies and external electric fields we aim to work towards better heterogeneous catalysts and more sustainable chemical processes.

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