Ferroelectrics: a pathway to switchable surface chemistry and catalysis

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Abstract

It has been known for more than six decades that ferroelectricity can affect a material's surface physics and chemistry thereby potentially enhancing its catalytic properties. Ferroelectrics are a class of materials with a switchable electrical polarization that can affect surface stoichiometry and electronic structure and thus adsorption energies and modes; e.g., molecular versus dissociative. Therefore, ferroelectrics may be utilized to achieve switchable surface chemistry whereby surface properties are not fixed but can be dynamically controlled by, for example, applying an external electric field or modulating the temperature. Several important examples of applications of ferroelectric and polar materials in photocatalysis and heterogeneous catalysis are discussed. In photocatalysis, the polarization direction can control band bending at water/ferroelectric and ferroelectric/semiconductor interfaces, thereby facilitating charge separation and transfer to the electrolyte and enhancing photocatalytic activity. For gas-surface interactions, available results suggest that using ferroelectrics as supports for catalytically active transition metals and oxides is another way to enhance catalytic activity. Finally, the possibility of incorporating ferroelectric switching into the catalytic cycle itself is described. In this scenario, a dynamic collaboration of two polarization states can be used to drive reactions that have been historically challenging to achieve on surfaces with fixed chemical properties (e.g., direct NO_x decomposition and the selective partial oxidation of methane). These predictions show that dynamic modulation of the polarization can help overcome some of the fundamental limitations on catalytic activity imposed by the Sabatier principle.

Keywords: Ferroelectrics, Catalysis, Photocatalysis, Switchable surface chemistry, Surface reconstructions, Novel scaling relations

1. Introduction

A polar surface arises when the electrical dipole associated with the bulk unit cell of a polar crystalline material has a non-zero component perpendicular to the surface i.e., $\vec{P} \cdot \hat{n} \neq 0$, where $\vec{P}$ is the bulk polarization vector and $\hat{n}$ the surface normal. The emergence of bulk polarization is a consequence of the offset between the centers of the positive and negative charges in each unit cell [1, 2]. If this polarization were uncompensated, a constant electric field would develop across the material with an energy cost scaling with the thickness of the material and rapidly becoming unphysically large for thick samples. The solution is to accumulate equal amounts of compensating opposite charges ($\sigma = \pm \vec{P} \cdot \hat{n}$) on the opposing polar surfaces to cancel the interior electric field so that the energy becomes independent of thickness. This can most simply be achieved through an electronic reconstruction: electrons or holes are transferred to the surfaces to compensate the polarization charge (Fig. 1) [3, 4, 5, 6, 7, 8, 9, 10]. Over timescales where atoms move and can migrate to or away from the surfaces, an additional avenue for compensation becomes possible: atomic reconstruction. Here, atoms are adsorbed or removed from the surfaces. These adsorbates or vacancies make available additional electronic states for electrons or holes that more favorably accommodate them compared to the energy bands of the stoichiometric surfaces. For pristine surfaces under UHV, the adsorbates are typically species found in the bulk, for example oxygen anion adsorption on the positive surfaces of polar oxides, while under ambient conditions a range of foreign species must also be considered. Such defects then accept the electrons or holes and lower the total energy of the surface, becoming ions in the process (in some cases charged species may adsorb directly). Thus, the net effect of atomic reconstruction is to add ions to the surface that balance the polarization with a surface charge density of opposite sign and cancel the electric field inside the material. It is worthwhile to note that there are scenarios where the polarization may not be entirely compensated. For example, ultra-high vacuum (UHV) can limit atomic reconstructions through adsorption while optical and thermal excitations in large bandgap ferroelectrics can be insufficient to fully compensate the polarization through electronic reconstruction [11, 12, 13]. Another mechanism by which ferroelectric surfaces may avoid reconstruction is through the formation of nanodomains of alternate polarization which can eliminate the net polarization [14].

Polar surfaces almost always minimize their energy through some variety of atomic reconstructions rather than through purely electronic reconstructions [3, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30]. These atomic reconstructions change the stoichiometry relative to the bulk termination which, in principle, can change the surface chemistry. Also, while the compensating charges eliminate the thickness-dependent component of the dipole, surface dipoles remain which can affect adsorption of polar molecules [31]. Ferroelectrics are a class of materials that have a spontaneous electric polarization vector (an order parameter) whose direction can be switched using an electric field and whose magnitude is temperature-controlled through the pyroelectric effect

[32, 33]. The modifications of ferroelectric surfaces due to the compensation of the surface charge density via adatoms, vacancies, surface dipoles and changes in surface electron density can all, in principle, alter the surface chemistry. Hence, ferroelectrics are promising candidates to achieve switchable and controllable surface physics and chemistry in which certain reactions can be turned on, off, or tuned.

Figure 1: Schematic illustration of two scenarios for a ferroelectric surface. a) Unphysical scenario: a large depolarizing electric field exists across the entire material created by the uncompensated surface charges stemming from ionic displacements along the polarization direction. b) electronic reconstruction by electrons or holes for positive or negative polarization $\vec{P}$ which results in zero net electric field inside the material.

Since the mid 20th century, the intriguing possibility of dynamically controlling surface chemistry and enhancing catalytic properties has turned ferroelectric and polar materials into the subject of numerous studies. Starting in 1952, Parravano observed anomalies in CO oxidation rates over ferroelectric sodium and potassium niobates near the Curie temperature of these materials (the second order transition temperature when the polarization vanishes) [34]. Next, in the 1960s, Stadler demonstrated that ferroelectric polarization can change the physical properties of supported metal films [35, 36]. The subject received renewed attention in the 1980s when Inoue et al. studied the effect of the substrate polarization on catalytic activity of supported metals and found higher CO oxidation rates for negatively poled surfaces, which they attributed to weaker CO adsorption for metal supported on the positively poled surface [37, 38]. In the same timeframe, dramatic effects of the polarization direction on adsorption on polar, but not ferroelectric, materials were demonstrated [39, 40]. Using Temperature Programmed Desorption (TPD) measurements to study the adsorption of oxygen-containing molecules that possess strong dipole moments, such as formaldehyde and formic acid, on polar ZnO surfaces, Akhter et al. showed strong interactions with the Zn-polar (0001) face, a weaker interaction with a non-polar face, and only a weak interaction with the O-polar (000 $\bar{1}$)

face [39]. Vohs et al. also studied ZnO polar surfaces using TPD and X-ray Photoelectron Spectroscopy (XPS) and showed that the Zn-polar crystal face readily oxidized both formic acid and formaldehyde while the O-polar face was unreactive [40].

The photocatalytic properties of ferroelectrics and polar materials have also attracted significant attention in the scientific community [41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60]. As far back as 1986, Inoue et al. studied photoassisted water decomposition on lead zirconate titanate (PZT) ceramics. In these experiments, 10-40 times higher H_2 production rates were observed for positive relative to negative polarization [42]. The main underlying mechanism was determined to be the polarization-dependent band bending close to the ferroelectric surface that facilitates the separation of the electron-hole pair and, depending on the polarization direction, directs either electrons or holes to the surface. Thus, in positive polarization, enhanced electron transfer to the surface promotes the hydrogen evolution reaction. A photocatalyst with a semiconductor/metal/ferroelectric structure was studied in which the semiconductor (TiO_2) exhibits a higher efficiency for hydrogen formation for positive polarization in contrast to negative polarization [43]. In succeeding work on the ferroelectric semiconductor lead strontium zirconate titanate ($Pb_{0.95}Sr_{0.05}Zr_{0.53}Ti_{0.47}O_3$), the difference in hydrogen evolution activity on the positive compared to the negative surface was increased by more than two orders of magnitude [44]. In 2001, Giocondi et al. studied photochemical oxidation and reduction reactions on the surface of ferroelectric $BaTiO_3$. For UV irradiation under aqueous solutions containing dissolved Pb^{2+} or Ag^+ cations, they observed accumulation of the oxidation product PbO_2 and the reduction product Ag on opposite polarization domains in patterns that reproduced the underlying ferroelectric domain structure. This demonstrated the ability of the ferroelectric to preferentially direct photogenerated electrons or holes to the surface depending on the polarization direction [61, 62].

Building on the results of Giocondi et al., the novel method of ferroelectric lithography was proposed in which ferroelectrics are utilized to fabricate multi-component nanostructures (oxide substrates, metal nano-particles and organic molecules) [63, 64, 65, 66, 67, 68, 69]. In this method, ferroelectric polarization in the substrate is manipulated to control local electronic structure and chemical activity and is patterned with electron beams or probe tips. By using photo reduction from aqueous solution, metal nanoparticles are deposited on predefined locations (see Fig. 2). Organic molecules can then react selectively on these nano-particles. This process can in principle be repeated to develop even more complex structures.

All ferroelectrics are necessarily pyroelectric so that their polarization magnitude is temperature dependent [70, 71]. Hence, heating or cooling a ferroelectric changes the balance of the surface compensating ions and surface polarization charges; as a result, the surface can temporarily find itself with extra charges for some time before it relaxes due to molecular adsorption/desorption or cancellation by the material's free carriers. As explained by Yun et al. [31], this leads to a sizable change in the surface dipole moment that can change surface

Figure 2: The domain orientation on PZT films visualized by scanning probe microscopy (a) and scanning electron microscopy (c) is correlated with the subsequent Ag photodeposition (b, d). Different microcontact stamps and subsequent photodeposition make grid like (e) and stripe like (f) silver patterns. Reprinted with permission from S. V. Kalinin, D. A. Bonnell, T. Alvarez, X. Lei, Z. Hu, R. Shao, and J. H. Ferris *Advanced Materials*, 16(9-10), 795-799.

chemistry. This effect is most noticeable in ferroelectrics with lower free carrier densities which strongly prefer external screening by adatoms (vacancies). This phenomenon has been exploited to create self-focusing, spatially stable, high energy (170 keV) electron beams using LiNbO_3 crystals in dilute gases [72], and to achieve “tabletop” nuclear fusion [73, 74, 75]. The basis of these experiments is the creation of a strong electric field near the ferroelectric surface which results from the temporary uncompensated charges on the surface of the ferroelectric created by heating or cooling [76, 77, 78, 79, 80, 81, 82, 83].

The seminal works briefly outlined above have motivated many fundamental studies on ferroelectrics and ferroelectric-supported thin films in recent years. In addition to many experimental studies, the development of better computational facilities, algorithms, software packages [84] and *ab initio* electronic structure methods, especially Density Functional Theory (DFT) and its derivatives, [85, 86, 87, 88, 89, 90], has led to a considerable number of theoretical studies in this field. Below, we review prominent recent experimental and theoretical results in the field of ferroelectric surface chemistry and provide an outlook on avenues that may potentially further advance this field. In particular, a strong potential benefit of ferroelectrics for catalysis can be their ability to deliver surfaces with dynamically switchable and tunable chemical properties. These systems may enable the realization of efficient processes for reactions such as NO_x direct decomposition or selective methane partial oxidation that have

been challenging for conventional catalysts operating within the restrictions of the Sabatier principle which governs catalysis by surfaces with static chemical interactions.

2. Bare Ferroelectric Surfaces

2.1. Surface Structure

As noted above, most polar surfaces experience atomic and electronic reconstructions that depend on the polarization magnitude and direction. Furthermore, as the band gap increases, atomic reconstructions become more favorable than electronic reconstructions [91]. Since the common ferroelectric materials all have bandgaps in excess of 3 eV [92, 93, 94, 95, 96], the expectation is that atomic reconstructions will dominate the charge compensation mechanism of undoped bulk materials at equilibrium. Within this context, Garrity et al. studied both electronically and atomically reconstructed PbTiO_3 surfaces using DFT [3]. They found that the positively polarized PbTiO_3 surfaces prefer to have either 0.5 ML O adatoms or 0.5 ML Pb vacancies, both electronegative defects, depending on the oxygen chemical potential; negatively polarized surfaces favor 0.5 ML electropositive oxygen vacancies. These atomically reconstructed, non-stoichiometric polar surfaces are in contrast to the non-polar paraelectric surface which prefers a stoichiometric state. Experimentally, a (4×1) reconstruction has been reported on the negative surface which is likely associated with arrays of oxygen vacancies on the surface [97]. Similar theoretical results have been reported by Mi et al. for BaTiO_3 surfaces [98]. They have shown that the presence of oxygen vacancies at the $\text{BaTiO}_3(001)$ surface preferentially stabilizes an inward pointing (negative) polarization. They used mirror electron microscopy (MEM) measurements [99], a variation of low energy electron microscopy (LEEM) with very low energy electrons that provides information on surface topography and work function, to confirm their theoretical results. We note that the surface structure of BaTiO_3 is complicated by a myriad of observed reconstructions that closely mirror those seen on paraelectric SrTiO_3 ; thus, many of the reconstructions are not primarily driven by charge compensation requirements [100, 101]. Nonetheless, Chen et al. have recently used an evolutionary algorithm approach to computationally study a large number of reconstructed surfaces and have found a significant polarization dependence in the phase diagram [102] of ferroelectric BaTiO_3 [103].

In 2008, Levchenko et al. used first-principle DFT calculations to study the surface reconstructions of ferroelectric LiNbO_3 (0001) as a function of polarization [19]. Their surface phase diagrams predicted that the positive surface is $-\text{Nb-O}_3\text{-Li}_2$ terminated (Li on top) and the negative surface is $-\text{Li-O}$ terminated (see Fig. 3). Their theoretical model, which indicates an excess of Li and O on the positive surface relative to the negative one, explains the experimental observations of Lushkin et al. [104] who discovered a difference in relative evaporation rates of LiO , Li and O_2 from LiNbO_3 surfaces depending on the polarization direction. This theoretical model is also consistent with

low energy ion scattering measurements that puzzlingly indicated that both the positive and negative surfaces were terminated by oxygen [105, 106]. Because low energy ion scattering is insensitive to Li, such ion scattering spectra reveal the surface O atoms with little evidence of Nb independent of the polarization. Separately, by using frequency-modulation atomic force microscopy (FM-AFM) [107, 108] to achieve atomic resolution on LiNbO_3 in an aqueous environment [109] in combination with DFT calculations, Sanna et al. showed that high temperature annealing drives off external adsorbates and unmask the intrinsic surface atomic reconstructions that lower the surface charge and energy [110]. Specifically, they observed a $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ reconstruction for the (000 $\bar{1}$) surface that they assigned to a superstructure of added Li-O groups on the surface.

Figure 3: Phase diagrams showing the thermodynamically stable surface terminations of negative (left) and positive (right) surfaces of LiNbO_3 (LN) (0001) as a function of Li and O chemical potentials. The terminations are labeled with hyphens. The unlabeled region on the left corresponds to a Nb-terminated surface. The black lines denote boundaries beyond which new bulk phases (shown on corresponding lines) start to precipitate on the surfaces. The physically important region where bulk LN is stable is within the trapezoid formed by the black lines. Reprinted with permission from S. V. Levchenko, and A. M. Rappe, Physical review letters, 100(25), 256101.

As explained above, both experiment and theory reveal a rich array of surface structures that depend on the ferroelectric polarization direction as well as the surrounding environment. Although the surface structures can be complex, a unifying theme is that in the absence of extrinsic compensating charges the surface stoichiometry adjusts to compensate the bulk polarization: oppositely poled surfaces are compositionally and structurally distinct [111, 112, 19]. Therefore, in addition to the electronic changes induced by polarization (induced free carriers and band-bending), structural and compositional differences can lead to a polarization-dependent surface chemistry on ferroelectric (polar) surfaces [113, 3, 114, 115, 29, 116, 117, 118, 119, 120, 121, 122].

2.2. Polarization dependent adsorption and desorption

In 2007, Yun et al. compared the adsorption of polar and non-polar molecules on oppositely poled, atomically reconstructed LiNbO_3 surfaces [123, 31]. The

results revealed that the interaction of polar molecules with the surface is dominated by electrostatic interactions with the surface dipole. As illustrated in the TPD results in Fig. 4, polar acetic acid desorption peaked roughly 100 K higher on the positive surface while non-polar dodecane desorption was independent of the polarization direction. The 100 K higher desorption peak temperature for acetic acid on the positive surface generally suggests substantially stronger adsorption on this surface. To quantify this difference, the desorption peak temperatures, T_P , were measured as a function of heating rate β . The data for dodecane were nearly identical for the two surfaces and as anticipated: the desorption activation energy was 0.80 eV per molecule and the pre-exponential 10^{15} s^{-1} , both values typical of large alkanes. Meanwhile, the data for the polar molecules acetic acid and 2-propanol were consistent with stronger adsorption on the positively poled surface (steeper slope) but also suggested desorption pre-exponentials at least 10 orders of magnitude lower than typically expected. When this is taken into account, the difference in desorption activation energies between the positive and negative surfaces becomes a modest 0.08 eV per molecule for acetic acid.

The anomalously low apparent desorption pre-exponential could be explained by a temperature dependent heat of adsorption. Because ferroelectric materials are also pyroelectric, large fields can develop at the surfaces of these materials when they are heated or cooled in vacuum as described in the Introduction. If no relaxation takes place, the net dipole would increase by roughly 285 eÅ/K during heating. Such a large change would alter how strongly polar molecules adsorb as the sample is heated but would have a negligible effect on a non-polar, weakly polarizable molecule such as dodecane. Subsequent work function measurements on 10 nm thick ferroelectric and pyroelectric PZT films on a metallic substrate supported this picture [124]. In these experiments, the work function reversibly increased by ≈ 300 meV when a positively poled film was heated from 300 to 400 K, consistent with the model that heating decreases the bulk polarization and leaves excess compensating charges on the surface that induce an inward pointing dipole across the PZT and increase the work function of the metal (See Fig. 5). It is easy to see how scaling these effects to the surfaces of bulk crystals can lead to enormous surface potentials that affect how strongly polar molecules interact with the surface. Taking this into account, the results indicate that the chemical interactions with the atomically reconstructed surfaces are weak and that intrinsic differences between the heats of adsorption on the oppositely poled surfaces exist but are not large.

Zhang et al. showed that differences between the behavior of oppositely poled surfaces cannot be solely due to electrostatic interactions [125, 126]. Using a combination of infrared microscopy and spatially resolved x-ray absorption near edge spectroscopy, in 2010 they studied the polarization-dependent adsorption of polar d-cysteine molecules on periodically poled LiNbO₃ during isothermal deposition from an aqueous 1M solution and observed preferential d-cysteine deposition on positive domains [126]. Since the deposition was isothermal and without illumination, it was concluded that the polarization dependent interaction between d-cysteine and the ferroelectric surface could not be

Figure 4: a) Comparison of acetic acid TPD curves for positively (top, red) and negatively (bottom, black) poled LiNbO₃ (0001). The sequence of curves illustrate the coverage dependence on the two surfaces; the vertical dashed lines highlight the difference in desorption peak temperatures. b) Dodecane TPD curves for several different coverages for positively (top, red) and negatively (bottom, black) poled LiNbO₃. The low temperature peak is due to multilayer desorption. The vertical dashed line shows that monolayer desorption has a peak at the same temperature on both surfaces, so that differences in the multilayer peak temperatures are due to the higher coverages on the negative surface. c) Redhead plots for acetic acid, 2-propanol, and dodecane on positively and negatively poled LiNbO₃ (0001) where β is the heating rate and T_P the desorption peak temperature. Adapted from Y. Yun and E.I. Altman, J. Am. Chem. Soc. 129 (2007) 15684.

due to the pyroelectric effect or photo-induced charges. They attributed this polarization dependent interaction to a dipole-dipole interaction between the surface and the molecule as well as to changes in surface chemistry related to polarization-dependent variations in Li/Nb concentrations. The latter conclusion was reinforced by their 2011 work in which they studied the chemisorption of two isomers of diiodobenzene on ferroelectric polymer surfaces where one of the isomers (1,2-diiodobenzene) was polar and the other (1,4-diiodobenzene) had zero net dipole [125]. They showed that the non-polar isomer preferentially adsorbed on positive domains at 150 K while the polar isomer strongly preferred the negative polarization. As a result of the polarization specific interaction of the non-polar isomer with the positive surface, they concluded that surface chemistry and not simply the surface dipoles (i.e., simple electrostatics) matters in these chemisorption processes. These results from Zhang et al. and Yun et al. on the interactions of non-polar molecules with the polar ferroelectric surface might initially appear contradictory. However, Yun et al. intentionally choose chemically inert dodecane as their non-polar molecule to isolate electrostatic contributions while the non-polar molecule chosen by Zhang et al., (1,4-diiodobenzene), is more reactive and hence its adsorption would be expected to respond more strongly to changes in surface structure and stoichiometry.

In 2009, Garra et al. studied the interaction of both H₂O and CH₃OH with

Figure 5: Plot of the change in work function of a SrRuO_3 (001) surface covered by 10 nm of positively poled PZT as the temperature was increased and decreased. Color online. Reprinted with permission from M.W. Herdich, H. Monig and E.I. Altman, *Surf. Sci.* 626 (2014) 53.

LiNbO_3 (0001) surfaces and discovered that this interaction was both coverage and polarization dependent [127]. The polarization dependence of the zero coverage desorption energies was estimated to be ≈ 0.05 eV per molecule higher on the positively poled surface. Three years later, Sanna et al. used *ab initio* DFT calculations to study water adsorption on LiNbO_3 (0001) surfaces and found that adsorption energies, binding configurations and molecular mobility change as a function of polarization [128]. Their results qualitatively agreed with the TPD measurements by Garra et al., with higher water adsorption energies on the positively poled surface, 1.28 eV per molecule on the positive versus 0.61 eV per molecule on the negatively poled surface. They mentioned that although their first principle calculations agreed qualitatively with the experiment, the computed polarization dependence was an order of magnitude larger than what was observed experimentally. In fact, this discrepancy is a general trend when one compares computational and experimental results on ferroelectrics, a fact that we will revisit below. In other work, Zhao et al. used the adsorption of 2-fluoroethanol on BaTiO_3 to assess the effect of polarization on reaction pathways [129]. The fluorinated ethanol adsorbs as an alkoxide that can react upon heating to produce acetaldehyde, ethylene, and adsorbed fluorine atoms which remain on the surface. Using TPD measurements, they observed a polarization dependent activation energy for acetaldehyde production which was ~ 0.04 eV per molecule higher on the positively poled surface.

The preceding works focused on adsorption energies and desorption rates. In 2008, Vohs et al. showed that polarization can also affect adsorption rates [130]. Specifically, they observed domain dependent sticking coefficients for CH_3OH and CO_2 on BaTiO_3 and $\text{Pb}(\text{Ti}_{0.52}\text{Zr}_{0.48})\text{O}_3$ surfaces using TPD and scanning surface potential microscopy, supported by first-principles calculations.

Also in 2008, Zhao et al. used TPD measurements to observe a polarization dependent sticking coefficient for ethanol on ferroelectric BaTiO₃ which was higher on positively poled surfaces [131]. The TPD peak shapes and the relative product yields were also polarization dependent suggesting that ferroelectric polarization may affect the intrinsic reactivity of the surface rather than simply changing the number of active sites. Recently, Stoflea et al. performed XPS and piezoresponse force microscopy (PFM) on PZT (001) single crystals and found that contaminants such as fatty acids, alcohols, and esters with oxygen containing anionic heads adsorbed preferentially on positive domains rather than negative ones [132].

As noted above, although the polarization direction can change the surface chemistry and modify adsorption and desorption for both polar and non-polar molecules [133], the magnitude of the effect in experiments is rather small and at most a few tenths of an eV. In parallel, the polarization dependences of binding energies computed by DFT are almost always overestimated in comparison [134, 128]. This difference is likely explained by the work by Garrity et al. who showed that both non-stoichiometric (atomically reconstructed) and stoichiometric (purely electronically reconstructed) surfaces show polarization dependent CO₂ and H₂O adsorption, but that the effect is much stronger on surfaces that have only undergone electronic reconstruction by free carriers [3]. In other words, the purely electronically reconstructed surfaces are not as stable as the atomically reconstructed ones and are thus more chemically active and more chemically differentiated. We offer the simple conclusion that the over-estimation of polarization dependence of adsorption energies is probably due to differences in the surfaces that are computationally modeled versus those that are stable under the conditions that the experiments are carried out.

2.3. Photocatalysis

As mentioned above, the photocatalytic properties of ferroelectrics have attracted much attention in the scientific community since the 1980s [135, 136, 137, 138, 139, 140]. In 2011, Schultz et al. studied the photochemical reduction of Ag from an aqueous solution on BiFeO₃ as a function of crystal and ferroelectric domain orientation. They observed that silver is preferentially reduced on domains with positive polarization. They also showed that the amount of reduced silver depends on whether the component of the polarization normal to the surface is positive or negative but is relatively insensitive to the crystal orientation [141]. In a study of photochemical reduction of Ag by Ba_{1-x}Sr_xTiO₃ ($x=0-1$), Bhardwaj et al. discovered that BaTiO₃ ($x=0$) selectively reduced Ag on positive domains. By continuously increasing x (which decreases the magnitude of the bulk polarization), they found a continuous change in reduction pattern from spatially selective to uniform [142]. They also discovered a local maximum in reactivity at $x=0.26$, near the cubic-tetragonal phase boundary: this corresponds to an anomalously high dielectric constant which results in a larger space-charge region [60, 143] and thus an increased reactivity. As mentioned above, one of the main mechanisms behind the enhanced photochemical reactivity of ferroelectric surfaces is the special (polarization dependent) band

bending that happens near the ferroelectric surface as a result of the internal electric fields associated with spontaneous polarization. In a comprehensive review of the subject by Li et al., four sources for this internal field have been presented: a) ferroelectric polarization, b) polar surfaces, c) p-n junctions [144, 145] and d) polymorph junctions [146]. As can be seen in Fig. 6, as a result of the band bending caused by these fields, the transfer of either holes or electrons to the surface can be facilitated. Thus, ferroelectric surfaces can exhibit spatially selective reducing or oxidizing photochemical activity.

Figure 6: Photogenerated charge carrier separation can be enhanced by internal fields: (a) ferroelectric polarization; (b) p-n junctions; (c) polar surfaces; and (d) polymorph junctions. (PC: photocatalytic active materials; SC: semiconductor). Reprinted with permission from L. Li, P. A. Salvador, and G. S. Rohrer, *Nanoscale*, 6(1), 24-42.

A recent study by Park et al. on a polarized particulate suspension (PS) system shows that the photocatalytic activity of $K_{0.5}Na_{0.5}NbO_3$ (NKN) for H_2 evolution improves by a significant factor of 7.4 due to polarization (relative to the paraelectric phase) [147]. They discover that the positively poled surface plays an essential role in promoting the photocatalytic activity. They attribute this to the improvement in the charge-separation caused by the photovoltaic effect and the efficient charge transfer characteristics promoted by band bending. The physical picture they propose begins with NKN being a n-type material so that one expects upward band bending (Schottky barrier formation) at the water-ferroelectric interface; however, the internal electric fields due to polar charge compensation near the surface induce downward band bending on the positive surface, so that the partial cancellation of the barrier facilitates electron transfer to the electrolyte and thus enhances the hydrogen evolution reaction (HER). Another benefit of ferroelectrics for photocatalysis, also pointed

out by Park et al., is the anomalously high photo voltages (APV) that can be achieved by these materials: the voltage output along the polarization direction can be vastly larger than the band gap of the ferroelectric material [148]. These properties have also raised interest in ferroelectrics for photovoltaic devices [149, 150, 151, 152, 153, 154, 155, 156, 157], where it has been shown that the switchable nature of ferroelectric polarization can lead to switchable photovoltaic properties [158, 159, 160, 161, 162, 163].

There has also been a number of studies that describe enhanced photocatalytic activity at domain and grain boundaries in ferroelectrics. In 2007, Jones et al. investigated the photo-reduction of silver salts on highly heterogeneous lead zirconate titanate (PZT) [164]. They showed that the greatest deposition rates occurred at grain boundaries, likely due to a combination of band bending and a positive electric field present at the grain boundaries that causes the electrons to migrate towards them [164, 165]. In 2009, Haussmann et al. studied single crystal LiNbO_3 and showed that photochemical reduction of elemental metals from ionic solutions on these surfaces was confined to ferroelectric 180° domain walls [166]. Sun et al. studied periodically poled lithium niobate (PPLN) and showed that for all above-gap-excitation wavelengths, deposition occurs on surfaces of either polarity as well as at the domain boundaries, but that the deposition density is greatest at the domain boundaries [11]. Sun et al. attribute the differences between the PPLN results and those for PZT and barium titanate (in which Ag deposition occurs predominantly on positive polarization [167, 142, 168]) to different polarization screening mechanisms. For materials such as PZT, the concentration of defects including oxygen vacancies is estimated to be relatively high so that the screening/compensation of the polar surface charge is done inside the material and leads to a sizable band bending. However, for materials such as lithium niobate which have a lower density of near surface defects, the band bending is weaker and the polarization charges are compensated primarily by external adsorbates. The external screening and weaker band bending of single crystal lithium niobate introduces an enhanced electric field at the domain boundary which leads to migration of electrons to the domain boundary and consequently enhanced Ag deposition along the domain boundaries. Sun et al. also show that high doses of oxygen implantation increases the defect concentration and changes the screening mechanism from external to internal, after which the deposition pattern becomes more similar to photo-deposition of Ag on PZT [169].

3. Ferroelectrics modified by transition metals

Despite the success of bare ferroelectric materials in aqueous phase photocatalysis, gas phase heterogeneous catalysis using ferroelectrics has been less promising since the effect of the polarization on adsorption energies was found to be small. This is not surprising since although the polarization surface charge density ($\sigma = \vec{P} \cdot \hat{n}$) is large in canonical ferroelectrics and is in the range of 0.5-1.0 electrons per surface unit cell, over time the ferroelectric surface becomes passivated through atomic reconstructions and is rendered less reactive. Hence, even

though first principles calculations on electronically reconstructed surfaces show pronounced polarization dependent behavior, such a surface phase is not easily accessible when the surface has time to relax to its thermodynamically preferred state. One way to avoid this problem is to try to combine the surface reactivity of transition metals with the polarization dependent properties of ferroelectrics. Here, one supports an ultra-thin transition metal film on a polar or ferroelectric substrate in order to modulate the transition metal surface chemistry through the substrate polarization. A specific example is the 1988 work by Didziulis et al. on Cu/ZnO [170] which showed that although CO chemisorption on highly dispersed Cu on the Zn-polar (0001) surface and the non-polar ($10\bar{1}0$) surface is very similar to CO chemisorption on bulk Cu, it is much weaker for Cu on the O-polar ($000\bar{1}$) surface. This approach has also been applied to aqueous phase photocatalysis [42]. This overall idea has provided a significant avenue of research into novel and potentially switchable surface chemistry and catalysis in the last few decades.

3.1. Polarization dependent adsorption and desorption

In 1990, Roberts et al. studied CO adsorption on Pt overlayers placed on different substrates: non-polar $\alpha - \text{Al}_2\text{O}_3$ (0001), positively polarized ZnO (0001), and negatively polarized ZnO ($000\bar{1}$) [171]. Using Auger electron spectroscopy (AES) and transmission electromicroscopy (TEM), they observed that Pt grows as a 2D film at 300 K on both polar surfaces in contrast to Pt on the non-polar sapphire surface on which it tends to form 3D particles. Using transmission electron diffraction (TED), they also showed that Pt grows as an ordered overlayer on ZnO crystals. Heating the Pt/ZnO surfaces resulted in the formation of 3D Pt particles starting at ~ 650 K. The TPD curves for CO from high Pt coverages (>1 ML) and from Pt particles formed by heating thinner films were shown to be identical to CO from Pt on the non-polar sapphire surface. For submonolayer coverages prior to Pt particle formation, however, the TPD curves for positively polarized ZnO (0001) shifted down by ~ 60 K compared to Pt on negatively poled ZnO ($000\bar{1}$). They interpreted this shift as an indicator of a chemical interaction between Pt and the Zn^{2+} ions which are in direct contact on the (0001) surfaces. Subsequent work by Vohs and co-workers on Pd on ZnO (0001) and non-polar ($10\bar{1}0$) reinforced this conclusion [172, 173]. They found evidence of Pd-Zn alloy formation after heating above 700 K that was more pronounced on the Zn-polar face which in turn had a larger effect on CO adsorption on the metal.

In 2007, Kolpak et al. used DFT to study polarization effects on the surface chemistry of PbTiO_3 -supported ultrathin Pt films [174]. They studied chemisorption of a variety of molecules and atoms and discovered that flipping the substrate polarization dramatically changed the computed chemisorption energies of CO, O, C, and N and altered the reaction pathways for dissociation of CO, O_2 , N_2 , and NO. In particular, they suggested that Pt could be made to dissociate CO, a reaction that does not normally occur on Pt surfaces. They suggested that by exploiting the polarization effect, one can optimize the metal-molecule interaction to maximize activity (i.e., achieve the peak of the

well known “volcano plot” of activity versus binding energy) to make a more efficient catalyst [175, 176, 177, 178, 179]. The main issue with this scheme is that to see a significant effect the Pt film must be ultrathin. The polarization effect is strongest for a monolayer (~ 1 eV binding energy shift), and it becomes almost negligible for films four or more layers thick (> 1 nm thickness). Unfortunately, experimental endeavors to create such ultrathin transition metal films on ferroelectric oxides reveal a strong thermodynamic drive for the transition metals to form bulk-like crystalline nanoparticles. For such particles, the polarization effect essentially vanishes due to the weak coupling to the ferroelectric substrate. In 2009, Yun et al. studied the growth of ultrathin Pd layers on positively and negatively poled ferroelectric LiNbO_3 (0001) surfaces [180]. Using low energy ion scattering, they discovered that the Pd tended to form three-dimensional clusters on both positively and negatively poled substrates even at the lowest coverages. They also investigated the chemical properties of these Pd clusters using CO TPD, but found no sensitivity to the direction of substrate polarization. Lastly, they studied the electronic structure of the Pd clusters as a function of their size and observed no effect of the substrate polarization and a cluster size dependence that was characteristic of an inert support; e.g. $\alpha\text{-Al}_2\text{O}_3$.

In the same year, Zhao et al. studied the same system using a combination of Auger electron spectroscopy (AES) and TPD [181]. They found that at 300 K, vapor-deposited Pd films grew in a layer-by-layer fashion on the negatively polarized LiNbO_3 (0001) surface, in contrast to the positively poled surface where they formed 3D clusters for otherwise identical growth conditions. They attributed this difference to the different interaction energies between Pd and the positive and negatively poled surfaces due to differences in the composition of these surfaces. They also studied the thermal stability of these systems: even on the negatively poled surfaces, the Pd film started to agglomerate into 3D particles at ~ 425 K. In 2011, Kim et al. used DFT and kinetic Monte Carlo simulations to study the same Pd on LiNbO_3 (0001) system [114]. For positive polarization, they found that Pd favored a clustered configuration, while for negative polarization Pd adsorbed in a more dispersed pattern due to suppression of diffusion and agglomeration. They traced back this disparity to the different adsorption geometries of Pd on LiNbO_3 due to the differing atomic reconstructions of the positive and negative surfaces [19]. They explained that for the negative surface, a strong bond between Pd and extra surface O led to a larger energy barrier for diffusion and agglomeration. Because formation of large Pd clusters is thermodynamically favorable on LiNbO_3 surfaces regardless of polarization state, they noted that it would be difficult to reversibly switch the Pd catalytic activity using ferroelectric polarization [114].

3.2. Photocatalysis

Several groups have sought to enhance the photocatalytic activity of ferroelectrics by adding transition metal catalysts. In 2013, Cui et al. studied the photocatalytic activity of BaTiO_3 by measuring the decomposition rate of the

typical dye molecule Rhodamine B under simulated solar light [182]. They observed that increasing the fraction of the material in the ferroelectric tetragonal phase through annealing tripled the photocatalytic catalytic activity. They also discovered that photochemical deposition of nanostructured Ag on the ferroelectric substrate significantly increases the photocatalytic activity of the material for organic decomposition reactions (see Fig. 7). Recently, Su et al. studied the novel photocatalytic properties of nanoscale ferroelectric BaTiO₃ [183]. The nanoscale BaTiO₃ has a large surface area which benefits catalysis, but the ferroelectric polarization of the nanoparticles is reduced compared to the bulk. By comparing behaviors above and below the Curie temperature, they showed that ferroelectricity could enhance the photocatalytic activity. They also discovered that coating BaTiO₃ with Ag can enhance the photocatalytic activity even further (>100%). They attributed this enhancement to the combined benefit of ferroelectricity, synergistic effects, local surface plasmon resonances, and specific charge-transfer kinetics in the Ag-BaTiO₃ hybrid nanoparticles. There have also been a number of studies on decorating BiFeO₃, one of the most promising multiferroic materials [184, 185] with a relatively narrow bandgap that may prove useful for visible-light-driven photocatalysis [186, 187, 188, 189], with Au and Ag nanoparticles [190, 191]. A remarkably enhanced photocatalytic behavior, relative to the bare BiFeO₃, was reported for both cases.

Figure 7: Photodecomposition profiles of the dye molecule Rhodamine B with different catalysts under illumination: dye concentration normalized to the initial concentration versus time. Catalysts containing more tetragonal ferroelectric BaTiO₃ after annealing show higher activity, especially when modified by Ag nanoparticles. Reprinted with permission from Y. Cui, J. Briscoe, and S. Dunn, *Chemistry of Materials*, 25(21), 4215-4223.

4. Oxides on Ferroelectrics

As explained in the previous section, key difficulties with enhancing ferroelectric reactivity by adding transition metals are that (i) the maximum effect is achieved in monolayer films and rapidly tapers off with thickness, and (ii) the

lack of wetting leads to the formation 3D transition metal nanoparticles on the ferroelectric surface; the nanoparticles, being primarily bulk like, couple only weakly to the ferroelectric. An alternate idea is to deposit chemically active metal oxide films on oxide ferroelectrics. Since they belong to the same class of materials and have lower surface tensions than transition metals, ultrathin oxide thin films can be grown more easily and with higher stability on oxide ferroelectric surfaces. In particular, recent advances in epitaxial growth methods, e.g., Molecular Beam Epitaxy (MBE) [192, 193, 194] and Atomic Layer Deposition (ALD) [195, 196, 197, 198], have made it possible to form structurally well-defined complex transition metal oxides of controlled thickness on ferroelectrics. In addition, metal oxides usually have longer screening lengths than transition metals which can enhance the coupling to the substrate’s polarization and extend the impact of the ferroelectric to at least several atomic layers [199, 115].

In the last few decades, numerous experimental and theoretical studies have examined the effects of ferroelectric substrates on the physics and chemistry of thin oxide films. For example, Ahn et al. studied the ferroelectric field effect in epitaxial SrCuO_2 and SrRuO_3 thin films on PZT and found reversible and nonvolatile resistance changes approaching 10% for 30 Å thick films when the ferroelectric polarization was reversed [200, 199]. This modification was related to the change in the number of free carriers in the conduction bands of the thin films. In principle, such changes in the occupancy of bands near the Fermi level can also significantly affect surface chemistry and catalysis. In 2004, Zhang et al. demonstrated that the rates of oxidation and reduction reactions catalyzed by the surface of a SnO_2 nanowire (configured as a field-effect transistors) could be varied by manipulating the electron density in the wire by applying a gate voltage [201, 202]. A much larger effect can be expected due to the surface charge induced by ferroelectric polarization, instead of a gate voltage [203, 204, 205], as Ahn et al. pointed out [194]: even a moderate ferroelectric polarization leads to a huge surface charge density of $\sim 1.5 \times 10^{14}$ electron/ cm^2 and a concomitant large internal electric field of ~ 300 MV/cm. Further, the remnant polarization in a ferroelectric obviates the need for a gate voltage.

4.1. Polarization dependent adsorption and desorption

In 2013, Garrity et al. employed DFT calculations to study transition metal oxide monolayers of the form BO_2 (e.g., RuO_2) that can continue the ABO_3 perovskite structure of ferroelectric PbTiO_3 [3]. They found that the surface chemistry of these monolayers couples strongly to the ferroelectric polarization of the substrate; for example, the binding energy of oxygen decreases by 1 eV per atom when one flips the polarization direction from positive to negative. They proposed that this reversible chemistry can be used to capture CO_2 molecules in one polarization state and then release them in the opposite polarization state (i.e., as part of a CO_2 sequestration system [206, 207]). As described above, the polarization dependence of binding energies is much more significant on surfaces with purely electronic reconstruction when compared to those passivated by atomic reconstructions [3]. Recently, this theoretical work was extended

Figure 8: Schematic band structure of a $\text{BiFeO}_3/\text{TiO}_2/\text{H}_2\text{O}$ heterostructure with the ferroelectric polarization (P_s) of BiFeO_3 (a) pointing away from the $\text{BiFeO}_3/\text{TiO}_2$ interface, and (b) pointing towards the $\text{BiFeO}_3/\text{TiO}_2$ interface. The vacuum level, conduction band edge, Fermi level and valence band edge are denoted by E_{vac} , E_c , E_f , and E_v , respectively. The hydrogen, silver, and oxygen redox levels are indicated on the right. Reprinted with permission from Y. Zhang, A. M. Schultz, P. A. Salvador, and G. S. Rohrer, *Journal of Materials Chemistry*, 21(12), 4168-4174.

to similar monolayer systems, including CrO_2 on ferroelectric PbTiO_3 , and a significant coupling between the monolayer chemistry and the substrate polarization was observed [10]. For electronically reconstructed surfaces, dramatic changes, in some cases in excess of 4 eV per molecule, were seen in the binding energies of different molecules such as NO , NO_2 , CO , CO_2 and O_2 upon changing the substrate polarization direction. In addition, modifying these heterostructures with a thin SrTiO_3 buffer layer between the surface monolayer and the ferroelectric substrate could stabilize them against transition metal interdiffusion and nanocrystallite formation (i.e., monolayer wetting is stabilized). In contrast to transition metals, the thickness of the SrTiO_3 buffer layer has a very weak effect on the polarization dependent surface chemistry indicating that the substrate polarization propagates without hindrance through the buffer layer. This is primarily because SrTiO_3 is a strongly polarizable incipient ferroelectric

(quantum paraelectric) [208, 209] whose polarizability is further aided by the epitaxial strain enforced on it by the PbTiO_3 [210].

On the experimental side, Inoue, et al have studied O_2 and H_2 adsorption on thick, in excess of 30 nm, NiO and TiO_2 films on oppositely poled LiNbO_3 (0001) surfaces. For NiO they observed higher O_2 desorption activation energies for negatively poled substrates, by 0.57 eV/molecule, while for H_2 on TiO_2 they reported a 0.15 eV per molecule higher desorption activation energy for the positively poled substrate [211]. These effects were correlated with changes in conductivity upon adsorption and were interpreted in terms similar to the field effect described above for SnO_2 nanowires [201, 202]. Specifically, cation vacancies in NiO tend to make it a p-type wide bandgap semiconductor; on the negatively poled ferroelectric substrate, the positively charged holes are attracted to the interface, creating a band bending that facilitates charge transfer to adsorbed oxygen. An opposite effect was proposed to explain stronger adsorption of electropositive hydrogen on n-type TiO_2 on the positively poled substrate. Following up on this work, Inoue and co-workers took advantage of the piezoelectric properties of ferroelectrics [212] to modulate the polarization and thus chemical properties of NiO [213, 214, 215]. In these experiments, they launched surface acoustic waves (SAW) in LiNbO_3 beneath NiO films and observed a four to seven fold increase in CO oxidation rates along with a decrease in the reaction activation energy. It was suggested that the temporally varying polarization induced by the SAW caused the NiO surface to alternate between strong and weak adsorption at the same sites which promoted reactant adsorption and product desorption.

For the thick films and relatively inert substrates in the experiments outlined above, the adsorbate coverages were limited to a few percent of a monolayer. Recently, thin epitaxial layers of catalytically active Cr_2O_3 layers on oppositely poled LiNbO_3 (0001) substrates were prepared with the expectation that larger effects could be induced in thin layers of more reactive oxides [12]. Photoelectron spectroscopy data revealed no band offsets associated with expected interfacial dipoles or changes in the Cr oxidation state which was taken as evidence that the compensating charges in the form of oxygen vacancies or oxygen adatoms could migrate to the Cr oxide surface. Experiments, however, revealed no significant effect of substrate polarization direction on oxygen adsorption.

4.2. Photocatalysis

Motivated by the need to increase the stability of perovskite ferroelectrics in aqueous solutions to make them useful for photoelectrocatalysis, Burbure et al. studied the photochemical behavior of titania films on BaTiO_3 substrates [216]. The reactivity was quantified by measuring the rate of silver reduction. As with the bare ferroelectric, the reaction products were spatially distributed in patterns consistent with the ferroelectric domain structure, in this case buried beneath the non-ferroelectric film. The photochemical reactivity was characterized not only as a function of ferroelectric domain orientation but also of the titania phase and orientation [217]. Among the surfaces examined, the bare BaTiO_3 substrates had the highest reactivity, 15 nm thick anatase films the

next highest, while thick (110) rutile films were the least reactive. Although the bare BaTiO_3 was the most active, this work demonstrated that oxide thin films can protect the ferroelectric surface against corrosion and leaching while still benefiting from the ferroelectric’s enhanced electron-hole separation and spatial separation of oxidation and reduction sites.

In 2011, Zhang et al. studied the photocatalytic activity of $\text{TiO}_2/\text{BiFeO}_3$ heterostructures under visible light [218] also using Ag reduction as a measure of the activity. Their work explained how the band bending direction inside the BiFeO_3 at the interface with TiO_2 changes as a function of polarization and how this facilitates the transfer of electrons to TiO_2 in positive polarization and suppresses it in the opposite polarization (see Fig. 8). Consequently, the Ag reduction pattern mimics the BiFeO_3 domain structure. Subsequently, Li et al. studied the photocatalytic hydrogen production activity of heterostructured ceramic powders that consisted of nanostructured TiO_2 surrounding microcrystalline $(\text{Ba},\text{Sr})\text{TiO}_3$ cores (see Fig. 9) [219, 146]. They demonstrated much higher hydrogen production rates for these heterostructures in water/methanol solutions than for each of the components alone; a similar result has been published on nanostructured TiO_2 surrounding PbTiO_3 cores [220]. A recent DFT study by Lee et al. on TiO_2 /ferroelectric heterostructures also shows that the ferroelectric substrate can strongly reduce rate-limiting barriers and significantly improve the oxygen evolution reaction (OER) relative to unsupported TiO_2 anatase [221].

Both theory and experiment suggest that photocatalytic properties of metal oxide thin films can be significantly enhanced by a ferroelectric substrate due to band bending and charge transfer to the surface. In addition, the chemical stability of the oxide films in aqueous environments in combination with the ability to transport photogenerated carriers through the oxide makes it possible to exploit the charge separation properties of the ferroelectric to improve photocatalytic performance.

5. Including ferroelectric switching in catalytic cycle

In this section, we aim to provide more insight into the use of ferroelectric polarization and its coupling to strain, temperature or electric fields to enhance catalytic activity in a *dynamic* manner. This in turn may permit one to move beyond some of the fundamental limitations imposed on catalytic activity when considering only static and equilibrated surfaces. As discussed above, the use of ferroelectric surfaces directly or as supports can lead to interesting and enhanced surface chemistry and catalysis. A potentially interesting way to exploit ferroelectrics is to create reversible and switchable chemistry in some dynamic or cyclic manner. We note that, for many good experimental and practical reasons, most prior studies have focused on surfaces with fixed polarization states. Usually, the interesting chemistry happens for one polarization state while the opposite polarization state is used as a reference to indicate the extent of the polarization effects. Or in other cases, each polarization state is

Figure 9: Bright field TEM images of a heterostructured particle composed of a microcrystalline-BaTiO₃ core and nanostructured-TiO₂ shell annealed at (a, b) 600°C and (c, d) 400°C. The entire particles are shown in (a, c), and higher magnification images of the coating are shown in (c, d). Reprinted with permission from L. Li, G. S. Rohrer, and P. A. Salvador, *Journal of the American Ceramic Society*, 95(4), 1414-1420.

inspected separately. Here, we discuss recent attempts to combine the activity of both polarization states in a cyclic manner.

In 2015, Kakekhani et al. proposed a cyclic catalytic scheme employing both polarization states where both are equally important parts of the cycle [10]. Beyond the creation of novel catalysts, another motivation for this work was to try to overcome some of the limitations on catalytic activity imposed by the Sabatier principle. The Sabatier principle is one of the cornerstones of catalysis [179]. It states that the efficiency of a fixed catalytic surface is maximized when the adsorbate-surface interaction strength is optimal: strong enough to drive the reactions forward but weak enough to permit the products to desorb. Hence, a large part of the effort in catalyst discovery and design has focused on fabricating and tuning material surfaces to make this interaction as optimal as possible (i.e., near the top of the ubiquitous “volcano plots”) [179, 222, 223, 224, 225]. The Sabatier principle highlights an unavoidable compromise between adsorption and desorption and imposes a fundamental limitation on catalytic activity of a given, fixed surface. Kakekhani et al. proposed that, in principle, exploiting ferroelectric polarization in a cyclic manner and using both polarizations allows one to overcome some of these limitation [10]. The basic idea is to use ferroelectric polarization to switch between one surface state with strong adsorption potential and a second surface state with strong desorption potential where the two surface states are controlled by direction of the substrate

Figure 10: Proposed catalytic cycle on CrO₂ monolayers supported on PbTiO₃ for NO direct decomposition into N₂ and O₂. In each case, the polarization direction is indicated by gray arrows. The green arrows show adsorption and desorption of the molecules. The cycle is begun from a clean and pristine positively poled surface and through multiple steps (after effectively dissociating 2 NO molecules into N₂ and O₂) returns to this state. Reprinted with permission from A. Kakekhani and S. Ismail-Beigi, ACS Catalysis 2015 5 (8), 4537-4545.

polarization (i.e., the substrate order parameter).

They considered a class of systems that consisted of a chemically active transition metal oxide (XO₂) surface monolayer (as a continuation of the ferroelectric perovskite structure) followed by a SrTiO₃ (STO) buffer layer (whose thickness ranged from 1 to 5 unit cells) on top of a ferroelectric PbTiO₃ substrate. Here, the STO buffer stabilizes the XO₂ surface monolayer against bulk nanocrystallite formation and transition metal interdiffusion. The transition metal X is chosen based on the specific reaction of interest [10]. For example, their work focused on NO_x direct decomposition, which has been a lasting challenge for conventional catalysis and the automotive emission control industry [226, 227, 228, 229, 230], and CO oxidation. Their calculated results showed that both CrO₂ and RuO₂ surface monolayer could simultaneously and efficiently catalyze these two reactions when implemented as part of the proposed cyclic scheme (see Fig. 10). In this approach, the fact that ferroelectric surfaces prefer to atomically reconstruct is no longer an unfavorable or limiting factor for enhanced surface chemistry. Instead, by dynamically switching the polarization, one actually exploits the thermodynamic drive towards atomic reconstructions to drive desired reactions for each surface state. The corresponding energy landscape diagram for this cycle for the case of a CrO₂ monolayer is shown in Fig. 11. Kakekhani et al. explained their computed binding energy trends by a generalization of the canonical d-band model for transition metals [231, 232, 233]

Figure 11: Energy landscape diagram for the proposed catalytic cycle on CrO_2 monolayers supported on PbTiO_3 for NO direct decomposition into N_2 and O_2 . The two arrows indicate the direction of the polarization in each part of the cycle: on the left is positive (up) polarization (parallel to the surface normal vector), while on the right is negative (down) polarization (antiparallel to the surface normal vector). The dashed gray line indicates the point in the cycle at which the polarization is flipped. Horizontal plateaus locate local minima, circles represent transition states as highlighted by the $\ddagger$ label. The reference energy is that of two NO molecules in the gas phase above a 2×2 CrO_2 - PbTiO_3 surface in positive polarization. Reprinted with permission from A. Kakekhani and S. Ismail-Beigi, ACS Catalysis 2015 5 (8), 4537-4545.

to metal oxide surfaces combined with charge transfer effects. As pointed out by Kakekhani et al., a secondary benefit of such a scheme is that the surface periodically goes through a strong desorption phase in which the poisoning atoms and molecules (e.g., SO_2) desorb [10]. We note that other work (presently under review) theoretically proposes cyclic enhancement of catalytic CO_2 dissociation to CO and oxygen using ferroelectric polarization for ultrathin films of ZnO on PbTiO_3 [115]. The experimental challenge is now to create and cycle such surface systems. The potential payoff is the creation of a switchable and/or tunable set of catalysts.

6. Outlook and conclusions

The effect of ferroelectric polarization on surface physics and chemistry has been studied for more than six decades [234]. The above survey of this field has shown that ferroelectric polarization can affect the adsorption energies, adsorption modes, and reaction rates of a variety of polar and non-polar molecules. These observations hold for both bare ferroelectric surfaces as well as ferroelectric substrates that support thin films of metals or metal oxides. In this final section, we take a broader view of current challenges in surface catalysis design to see how ferroelectrics may potentially contribute to overcoming a number of the challenges.

Surface catalysis based on transition metals and their alloys has been one of the most important research fields in theoretical and experimental catalysis and chemistry [235, 236]. In addition to basic scientific discoveries, this field has had enormous impacts on daily lives, e.g., it has helped overcome the world hunger problem by introducing the Haber-Bosch process to efficiently break the

strong N_2 triple bond and synthesize ammonia which is the most important precursor for fertilizers [237, 238]. A significant breakthrough for transition metal catalysis in the last few decades has been the introduction of a predictive theory for catalysis based on a combination of the d-band model, activity maps and scaling relations [239, 240, 241, 242, 179]. Having efficient computational tools and a predictive theory has permitted computational scientists to design novel catalysts and computationally screen materials for a specific functionality, and then one can attempt to experimentally fabricate the promising candidates [243, 222, 244].

Among the many contributions of this descriptive theory has been the modification of the stability of Ni catalysts for steam reforming by the addition of gold and the mixing of cobalt and molybdenum in ammonia synthesis catalysts [245, 224, 246]. Scaling relations have been one of the foundations for understanding catalytic trends: these relations help by significantly reducing the number of potentially independent degrees of freedom (e.g., the full set of binding energies of the products and intermediates) in a chemical reaction to just a few descriptors [231, 247, 175, 248, 249, 250]. However, as Vojvodic and Norskov pointed out in a recent review, despite being extremely useful, scaling relations have also helped identify some of the limitations on the tunability of large classes of catalysts [251]. Figure 12 provides an example for the case of ammonia synthesis. Clearly, a much better catalyst for ammonia synthesis could be fabricated if one could circumvent or depart from the known scaling relations for (stepped) transition metal surfaces: the scaling relation has confined these surfaces to being far from maximally efficient. Due to this restriction, namely the reduced degrees of freedom stemming from the scaling relations, there are many reactions that cannot be fully optimized and thus suffer from inefficient catalysis. There are also some important reactions that currently have no effective catalysts (e.g., the partial oxidation of methane to methanol [252, 253, 254, 255] and the direct decomposition of NO_x [256]). The need for an extra degree of freedom that can take us away from the constraints of the scaling relation is clear.

We suggest that ferroelectrics may make an important contribution in this regard. Ferroelectric surfaces have an added degree of freedom which is the direction of the polarization below the surface. Furthermore, the polarization couples to multiple physical degrees of freedom which permits different pathways to modulate the polarization. For example, we mentioned above how acoustic waves may modify surface electronic properties through the piezoelectric effect [213]. However, piezoelectricity is not the only possibility: temperature can modify the polarization via the pyroelectric effect or, more obviously, one can use external electric fields to directly control the polarization. We note that some ferroelectrics are multiferroic: their magnetic properties are coupled to their electrical polarization [257, 258, 259], so that, in principle, one can also enlarge the list of external control knobs to include magnetic fields [260, 261, 262]. The overall logic is that a ferroelectric surface has added tunability because: (i) there is an order parameter (here the ferroelectric polarization) below the surface, (ii) the order parameter concerns charge degrees of freedom and thus

Figure 12: Ammonia synthesis rate as a function of nitrogen adsorption energy E_N and N_2 dissociation barrier E_{N-N} with energetics for stepped transition metal sites and the corresponding scaling relation line (dashed black-white) showing that E_{N-N} is a linear function of E_N , which prevents the metal steps from entering the optimum catalyst region (red area). The alkali-promoted scaling relation is given by the magenta line. b) Calculated rate as a function of a single descriptor of E_N . Reprinted with permission from A. Vojvodic and J. K. Norskov, National Science Review (2015): nww023.

can couple strongly to the surface chemistry, and (iii) the order parameter can be controlled by external knobs. In principle, this should permit one to shift the scaling relations in their appropriate phase space.

A second benefit of using ferroelectrics is the potential for dynamic or cyclic behavior [10]. Namely, instead of simply using the polarization to shift scaling relations, one can envisage sidestepping some of the fundamental compromises in the usual approach to catalyst optimization. To reiterate a point from the previous section, the Sabatier principle enforces a compromise situation for a fixed surface: maximum activity requires an optimal adsorbate-surface interaction strength that is neither too strong nor too weak [179]. However, if one could cycle the surface between multiple states with very different interaction strengths, some of the compromises could be overcome: adsorption and desorption do not have to be competing effects but both can be periodically enhanced or suppressed to drive the appropriate set of reactions or adsorption/desorption processes in sequences [10, 115]. The SAW experiments described above provide some evidence that such a mechanism is achievable [214, 213]. We surmise that the cyclic control of ferroelectric surfaces and their chemistry may open up entirely new ways to create and design catalytic materials and processes.

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