Defluorination and adsorption of tetrafluoroethylene (TFE) on TiO$_2$(110) and Cr$_2$O$_3$(0001)

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Here, we show that metal oxide surfaces catalyze the formation of intermediate defluorinated tetrafluoroethylene (TFE) radicals, resulting in enhanced binding on the corresponding metal oxide surfaces. We attribute the preferential adsorption and radical formation of TFE on Cr$_2$O$_3$(0001) relative to TiO$_2$(110) to the low oxygen coordination of Cr surface atoms. This hints at a possible dependence of the TFE binding strength to the surface stoichiometry of metal-oxide surfaces.

Being able to join dissimilar materials (cf., e.g., Refs. 1–4 and references therein) is a key enabling technology to innovative and sustainable materials design for industrial applications. Some notable examples include: polymer-metal composites for bio-prosthetics and medical tools$^{12}$; polymer-functionalized metal oxide surfaces for specialized applications$^{3–7}$; polymers passivating metal oxide defects to increase carrier efficiency for better optoelectronic materials$^{8,9}$; and polytetrafluoroethylene (PTFE) used as fluorine sources to form oxyfluoride surfaces and functionalize metal-oxides towards the realization of superconductors$^{10}$. All of these applications fundamentally start with polymer adhesion on metal surfaces.

Two of the most commonly used metals for industrial applications are titanium and stainless steel, due to their notable physical properties, e.g., being lightweight and less susceptible to corrosion. In actual applications, these metals are exposed to oxidizing agents in the environment such as O$_2$ or water vapor, hence, they still manifest a thin layer of metal oxide surface. For example, on stainless steel surfaces, a layer of Cr$_2$O$_3$ forms as a protective coating against further oxidation$^{11}$. Similarly, TiO$_2$ thin layers form on the surface of titanium, enhancing its biocompatibility for medical purposes$^{12}$. Studies also show that the formation of thin metal oxide surfaces enhances binding to other metals and insulating polymers through welding or irradiation of the surface$^{15–18}$. Here, we show the role of the reactivity of these thin metal oxide films to chemically bind with TFE.

In the following, we present results of our study on the adsorption of tetrafluoroethylene (TFE) on TiO$_2$(110) and Cr$_2$O$_3$(0001). We found TiO$_2$(110) inert and Cr$_2$O$_3$(0001) active to TFE (molecular) adsorption. This can be attributed to the nature of the surface metal atoms and the corresponding oxygen coordination. Furthermore, we found that defluorination of TFE promotes adsorption on both TiO$_2$(110) and Cr$_2$O$_3$(0001). These results indicate the role of the surface as a catalyst to form intermediate TFE radicals and promote adsorption on metal-oxide surfaces. Thus, the possibility of joining dissimilar materials (in this case polymer and metal-oxide surface).

Results and discussions

Molecular Adsorption of TFE on TiO$_2$(110) and Cr$_2$O$_3$(0001). In Fig. 1, we see weak (ca. − 0.07 eV, Configuration 1) molecular adsorption of TFE monomer on TiO$_2$(110) and strong (ca. − 1.38 eV, Configuration 1) adsorption on Cr$_2$O$_3$(0001). We find TiO$_2$(110) inert and Cr$_2$O$_3$(0001) active to TFE (molecular) adsorption. These results and observations could be compared with previous studies showing an inert TiO$_2$ towards fluorination from PTFE forming surface oxyfluorides$^{19}$. On the other hand, we find a relatively stronger binding for TFE adsorbed on Cr-terminated Cr$_2$O$_3$(0001), with the molecular plane tilted relative to the surface axis. We found that molecular adsorption of TFE on both metal oxide surfaces does not result in any significant
relaxation of the surface. However, the difference in the adsorption energy could be attributed to the difference in the surface oxygen (O)-coordination of the surface metal atoms (Ti and Cr).

In Fig. 2, by inspection, we see that the surface Ti on TiO$_2$(110) have higher O-coordination than the surface Cr on Cr$_2$O$_3$(0001). We attribute the difference in surface reactivity, i.e., adsorption preference, to the difference in surface metal–oxygen ratio. We define this ratio as the number of low coordinated surface metal ions to the fractional number of oxygen atoms bound to it, i.e., 3:7 for TiO$_2$(110) and 1:1 for Cr$_2$O$_3$(0001). To verify this, we have added an additional Cr termination on the surface of Cr$_2$O$_3$(0001) (4:3 Cr to O ratio) and found a stronger adsorption of TFE with a pronounced non-planar geometry. As expected, we can enhance TFE adsorption on TiO$_2$(110) by introducing oxygen vacancies (cf., e.g., Refs. 16−18, and references therein).

It requires energy to break the C–F bond of TFE and, in Fig. 1, we see an endothermic dissociative adsorption of TFE (i.e., Configuration 2, with dissociated C–F bond) on both TiO$_2$(110) and Cr$_2$O$_3$(0001), with respect to the molecular state (Configuration 1). However, upon surface relaxation, the total energy lowers, resulting in a rather exothermic adsorption for C$_2$F$_3$ on TiO$_2$(110) (1.39 eV) and Cr$_2$O$_3$(0001) (2.16 eV). As mentioned earlier, such surface relaxations are negligible in TFE molecular adsorption. The binding of C$_2$F$_3$ on surface O atom and the binding of F on surface metal atom (Ti and Cr) resulted in an upward (coordinate) shift of the interacting surface atoms. By comparison, we can see a greater upward shift of Cr and O towards the vacuum for Cr$_2$O$_3$, whereas a relatively smaller relaxation on TiO$_2$ upon adsorption of the defluorinated TFE (cf., Fig. 3). (Note that the energies from Configuration 0 to 2 on both TiO$_2$(110) and Cr$_2$O$_3$(0001) lowers after implementing van der Waals (vdW) correction).

The relative energy plots suggest that the presence of the metal oxide surfaces lowered the energy needed to break the TFE C–F bond. However, it requires 5.3 eV to dissociate one F from TFE in vacuum. To explore the possibility of a lowered TFE C–F bond dissociation barrier in the presence of metal-oxides, we implemented a simple dissociation model of TFE using the molecular counterpart of the metal-oxide surfaces. In Fig. 4, we show the calculated potential barriers from the molecular TFE state to the dissociated TFE state on Cr$_2$O$_3$ (ca. 1.39 eV) and TiO$_2$ (ca. 2.16 eV). It can be seen from the simple molecular model that C–F dissociation energy lowers in the presence of metal-oxides. These results indicate the role of the surface as a catalyst to form intermediate defluorinated TFE radicals. In the following, we focus on the adsorption of defluorinated radicals of TFE on Cr$_2$O$_3$ and TiO$_2$ surfaces.

Figure 1. TFE on TiO$_2$(110) and Cr$_2$O$_3$(0001) in 3 different configurations, viz., reference structure (0), molecular adsorption (1), and defluorinated adsorption (2) on the corresponding surfaces. Upper panel corresponds to the relative energies of optimized adsorbates on frozen surfaces. Lower panel corresponds to the relative energies with surface relaxation. (Note stronger TFE adsorption on Cr$_2$O$_3$(0001) than on TiO$_2$(110), having retained energy trend after implementing van der Waals (vdW) correction).
Upon defluorination (cf., e.g., Fig. 1, Configuration 2), the C_2F_3 creates a new bond with surface O atoms and the dissociated F atom adsorbs atop the adjacent transition metal atom. We also see a relatively more stable adsorption on Cr_2O_3(0001) than on TiO_2(110). This results in a higher charge population around the carbon end of C_2F_3 on Cr_2O_3(0001) than on TiO_2(110) (cf., Fig. 5). The relatively higher accumulation of charge from Cr_2O_3 (0.2 e higher) results in a longer C=C bond length (shown in Fig. 3) as compared to that on TiO_2. From the corresponding charge density difference distribution (cf., Fig. 6) electron contribution comes from both surface (oxygen and metal) atoms. We see a more pronounced participation of Cr in TFE radical bonding as compared to Ti shown by the charge gain region (yellow region) between C and Cr surface atom. By plotting the projected density of states (PDOS), after TFE radical bonding, we show a strong hybridization of the C p states with the d electrons of Cr. This is less evident in the case of TiO_2 where hybridization is mainly through the surface oxygen atom. As mentioned in the previous section, the surface metal–oxygen ratio influences metal-oxide surface reactivity towards TFE adsorp-

**Figure 2.** Top view of TiO_2(110) (left panel) and Cr_2O_3(0001) (right panel), with coordination numbers of surface and subsurface atoms indicated. Note the lower coordination number of the surface Cr atoms as compared to the surface Ti atoms.

**Figure 3.** Optimized structure for defluorinated TFE adsorption with the corresponding surface relaxation after adsorption. (+) refers to relaxation of surface atoms towards the vacuum and (−) refers to relaxation of surface atoms towards the bulk. The values are deviations from the clean surface configuration.
tion. From the TiO$_2$(110) geometry, we find the first Ti layer completely enclosed by the octahedral cage of O, resulting in a low surface Ti–O ratio. This accounts for the weak interaction of surface Ti towards C$_2$F$_3$. Next, we show in Table 1 the corresponding adsorption energies of CF, CF$_2$, CF$_3$, CF$_4$, C$_2$F, C$_2$F$_2$, C$_2$F$_3$ on TiO$_2$(110) and Cr$_2$O$_3$(0001). In general, defluorinated TFE radicals with intact C=C bond show stronger adsorption, and preference for adsorption on Cr$_2$O$_3$(0001). We also show that in most cases, radicals with low fluorine content manifest stronger binding on the oxide surfaces. These results indicate that chemical adsorption of the TFE monomer starts with defluorination and adsorption with an intact C=C.

Summary and conclusion
In summary, we have shown that defluorination is necessary to increase chemical bonding between tetrafluoroethylene (TFE) on TiO$_2$(110) and Cr$_2$O$_3$(0001). The metal oxide surface catalyzes defluorination, resulting in the formation of intermediate radicals that bind strongly to the corresponding metal oxide surfaces. As expected, the reactivity of the corresponding metal oxide surfaces depends on the oxygen coordination of metal surface atoms. The surface Cr on Cr$_2$O$_3$(0001) has a lower fractional oxygen coordination as compared to the surface Ti on TiO$_2$(110). As a result, we find stronger bonding of TFE on Cr$_2$O$_3$(0001) than on TiO$_2$(110). This also indicates that introducing oxygen vacancies (cf., e.g., Ref.16–18, and reference therein), and non-ionizing radiations (cf., e.g., Ref.19 and references therein) to form intermediate radicals could promote binding of polymers to metals. These results should provide insights for better materials design, specifically towards polymer adhesion on metal-oxide surfaces.

Computational method. To study the adsorption of TFE and its fragments on TiO$_2$(110) and Cr$_2$O$_3$(0001), we performed density functional theory20,21 (DFT)-based total energy calculations22–26 using projector augmented wave (PAW) formalism and plane wave basis set (cutoff energy of 550 eV), and Perdew–Burke–Enzer-
hof (PBE) generalized gradient (GGA) exchange correlation functionals\textsuperscript{27,28}. We adopt the Monkhorst and Pack method to perform the Brillouin zone integrations, with (9 × 9 × 1) special \( k \)-points\textsuperscript{29}. To model TiO\(_2\)(110) and Cr\(_2\)O\(_3\)(0001), we used periodically repeated slabs of (2 × 1) and (1 × 1) surface unit cells, respectively, separated by 15 Å thick vacuum region along the surface normal. The lattice constant obtained upon structural optimization for Cr\(_2\)O\(_3\)(0001) is 5.03 Å and the lattice constants for TiO\(_2\)(110) are 2.97 Å and 6.59 Å. These structural geometries are in good agreement with experimental and theoretical studies\textsuperscript{30–32}. Each slab consists of 2 layers (7 atomic planes) of O-Ti-O and Cr-O-Cr. In the case of Cr\(_2\)O\(_3\), we used a Cr terminated surface as it was found to be more stable than other terminations\textsuperscript{30}. We performed geometric optimization considering energy convergence of less than 10\(^{-5}\) eV and residual forces below 0.01 eV/Å. For the molecular and dissociated adsorption of TFE we implemented both frozen and relaxed surface calculations. We implemented van der Waals correction using DFT-D2 incorporated in the VASP code.

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![Figure 6](image-url). Charge density difference for C\(_2\)F\(_3\)+F on TiO\(_2\)(110) (upper left panel) and Cr\(_2\)O\(_3\)(0001) (upper right panel). Yellow to red region indicates electron gain. Light blue to dark blue region indicates electron loss. Projected density of states for C\(_2\)F\(_3\)+F on TiO\(_2\)(110) (lower left panel) and Cr\(_2\)O\(_3\)(0001) (lower right panel).

| TFE Radical | \( E_{ad} \) [eV] on TiO\(_2\)(110) | \( E_{ad} \) [eV] on Cr\(_2\)O\(_3\)(0001) |
|-------------|--------------------------------|---------------------------------|
| CF          | −2.05                         | −4.48                          |
| CF\(_2\)    | −0.47                         | −2.75                          |
| CF\(_3\)    | −1.66                         | −2.2                           |
| CF\(_4\)    | −0.05                         | −0.63                          |
| C\(_2\)F    | −2.34                         | −5.31                          |
| C\(_2\)F\(_2\) | −2.42  | −5.07                          |
| C\(_2\)F\(_3\) | −2.02  | −2.53                          |

Table 1. Adsorption energy of defluorinated TFE radicals on Cr\(_2\)O\(_3\)(0001) and TiO\(_2\)(110).
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