Preferential Growth of Pt on Rutile TiO$_2$

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(Dated: June 18, 2018)

The characterization of Pt/TiO$_2$ (Degussa P25) catalyst system using atomic resolution Z-contrast images and electron energy loss spectroscopy in the scanning transmission electron microscope has recently revealed that Pt particles have a strong tendency to nucleate on the rutile phase of TiO$_2$ rather than anatase. Comparative ab initio pseudopotential calculations for Pt and Pt$_2$ on the stoichiometric and reduced TiO$_2$ surfaces, and oxygen vacancy ($V_O$) formation energies are performed to address the microscopic origin of this finding. The results, which show that Pt actually binds more strongly to anatase surfaces, indicate that the selective growth of Pt on rutile must be controlled by the lower formation energy of $V_O$ on rutile, and possibly by the stronger tendency of $V_O$ sites on rutile to trap large Pt clusters compared to anatase.

The fundamental and technological importance of TiO$_2$, stemming to a large extent from its wide spread use as a catalyst and catalyst support, has made it the subject of many experimental and theoretical studies over the last decade.[1] As one of the most active catalysts for CO oxidation reactions and photocatalysis, in addition to being the prototype system for the strong-metal-support-interaction (SMSI) phenomenon, [2] Pt/TiO$_2$ has recently received particular attention. The catalytic properties of Pt/TiO$_2$ and the occurrence of SMSI has a strong dependence on the phase of TiO$_2$ (rutile versus anatase). For example, it was recently shown that anatase titania palladium supported catalyst presents SMSI at low H$_2$ pre-reduction temperatures, while rutile does not.[3] It is also well known that anatase is more efficient than rutile as an oxidative photocatalyst. [4] The presence of a small amount of rutile, however, such as in commercial mixed-phase titania samples results in an unusually high activity.[5] A fundamental comparative study of the interaction of Pt with both rutile and anatase TiO$_2$ surfaces will, therefore, contribute to our understanding of the catalytic properties of this system and the occurrence of SMSI.

Recently, using a combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM), we examined the atomic and electronic structure of the Pt/TiO$_2$ interface. [6] The experiments were performed on a commercial mixed-phase titania sample, known as Degussa P25, which is composed of about 80 % anatase and 20 % rutile. We observed rather unexpectedly that Pt particles were not uniformly distributed over the titania particles, but showed a selective distribution, as shown in Fig. 1(a). The oxygen–K edges of these specific particles [Fig. 1(b)] combined with the reference O-K edge EEL spectra of rutile and anatase TiO$_2$ [Fig. 1(c)] revealed that the densely Pt populated titania particles were of the rutile phase while the barely populated ones were of anatase. This finding was consistently observed throughout the samples, and also confirmed with the characteristic peak at around 14 eV in the low loss EELS. [4, 5] Similar observations were reported earlier for Ru-RuO$_x$/TiO$_2$, Ir/TiO$_2$, and Au/TiO$_2$ systems. [7] Motivated by these interesting experimental observations, in this paper, we present results from large-scale ab initio calculations which provide possible explanations for the observed preferential growth of Pt particles on rutile rather than anatase.

Our calculations for the atomic and electronic structures of single Pt atoms and Pt$_2$ dimers on the stoi-
chiometric and reduced rutile and anatase TiO₂ surfaces were performed using the pseudopotential total energy method in a slab geometry. The specific surfaces chosen for this study, (110) for rutile and (101) for anatase, are the most energetically stable surfaces of each phase forming a large portion of surface area in Wulff construction studies. We used ultrasoft pseudopotentials with a cutoff energy of 300 eV, 1 × 2 × 2 Monkhorst-Pack k-point grids, and Perdew and Wang parametrization of the generalized gradient approximation. Increasing the cutoff energy to 400 eV and the k-point grid to 2 × 4 × 4 had no appreciable effect on the results. We made an extensive study of the effects of spin polarization effects and found them to be negligible for the Pt/TiO₂ system. After a systematic study and comparison with larger slabs (checked up to 10 layers in 2 × 1 surface cells), we found a 4-layer asymmetric slab, in which the two bottom layers are kept at bulk positions, to be the smallest good representation of the surface with and without Pt atoms on the surfaces. We used a vacuum region of 11-12 Å. To model the metal atoms on the rutile and anatase surfaces, we used large surface unit cells, 3 × 2 (stoichiometric) and 4 × 2 (reduced), resulting in 144 and 192 atoms per slab, respectively. More details about the calculations and convergence tests on rutile (110) can be found in Ref. 11.

A reasonable explanation for the preferential growth of Pt on rutile could come from the differences in the binding energies (BEs) of Pt atoms to the rutile (110) versus anatase (101) surfaces. That is, based on the experimental results one might expect that Pt would bind more strongly to stoichiometric and/or reduced rutile (110) compared to anatase (101) surfaces. In order to test this hypothesis, we first investigated the binding of a single Pt atom to the stoichiometric rutile (110) and anatase (101) surfaces (Table I). As reported previously, we find the most favorable position for Pt adsorption on the stoichiometric rutile surface as the hollow site [Fig. 2(a)] with a BE of $E_{S,Rut} = 2.21$ eV. At this site Pt binds to a five-fold coordinated Ti atom (Ti5c) and a bridging oxygen. On the stoichiometric anatase surface, the most favorable site for Pt adsorption is the equivalent site to the hollow position found above [Fig. 2(b)], as Pt binds to the under-coordinated Ti (Ti5c) and O atoms as well as six-fold coordinated Ti6c. The calculated BE on the stoichiometric anatase surface is $E_{S,Ana} = 2.87$ eV, which is surprisingly higher by 0.66 eV compared to $E_{S,Rut}$. By itself, this result would suggest that on stoichiometric surfaces, a Pt atom would prefer to bind to anatase rather than rutile, which is contrary to our experimental finding of preferential growth on rutile.

Since oxygen vacancies are known to play an important role in the anchoring of metal atoms on TiO₂, we also examined the binding of Pt atoms to the reduced rutile and anatase surfaces (Table I). As expected, we find the most favorable adsorption on both surfaces to occur at the substitutional (oxygen vacancy) site [Figs. 2(c) and (d)]. The calculated BEs of $E_{R,Rut} = 3.59$ eV and $E_{R,Ana} = 5.05$ eV are considerably larger compared to those on stoichiometric surfaces. However, the surprising result of even stronger preference of Pt to bind to reduced anatase (101) rather than reduced rutile (110) by a significantly large BE difference of 1.46 eV is again contrary to our experimental finding.

At this point, it is natural to ask why Pt binds more strongly to anatase (101) surfaces than to rutile (110). We first note that our analysis of the charge density profiles to examine the nature of the bonding of Pt to rutile and anatase surfaces has not revealed a significant difference between the two phases. The reasons behind the stronger binding of Pt to anatase in comparison to rutile can be more easily understood from the different coordinations of Pt and the resulting effect of these on the Pt $d$-band. On the stoichiometric rutile (110), Pt bonds to only one bridging oxygen (at 2.01 Å) and one 5-fold coordinated Ti atom (at 2.50 Å), as shown in Fig. 2(a). On the stoichiometric anatase (101), on the other hand, Pt fits well (with a very small protrusion above the surface) into the large spacing between two 2-fold coordinated oxygens, two 5-fold coordinated Ti, and two 6-fold coordinated Ti atoms [Fig. 2(b)]. In addition to the increased coordination of Pt, the other significant difference between the two cases is the Pt-Ti interatomic distance, which increases to an average of 2.78 Å on anatase (101). Examination of the Pt-Ti interatomic distance in various PtTi compounds, such as in B2 and B19 structures, shows that the preferred nearest-neighbor Pt-Ti distance is near 2.75 Å (the same analysis for Pt oxides shows a preferred Pt-O bond near 2.0 Å). Therefore, on anatase (101) Pt not only has a higher coordination than on rutile (110), which indicates...
increased binding, it can also position itself at preferred distances from both O and Ti due to the larger spacings between the bridging oxygen rows. This stronger interaction of Pt with anatase (101) surface manifests itself in the $d$–partial density of states (PDOS) around the Pt atom as shown in Figs. 3(a) and 3(b). The stronger hybridization of the Pt $d$–states with Ti pushes the occupied states (around $-2$ eV in rutile) down to much lower energies in anatase, while increasing the energy of the unoccupied states (near $0.6$ eV on rutile) to higher energies in anatase, as shown by the arrows in Fig. 3(a).

The reason behind the stronger binding of Pt to the reduced anatase (101) compared to rutile (110) is the difference in the coordination of the two Ti atoms bonded to the Pt atom. On rutile, Pt sits equidistant from two Ti6c atoms at 2.39 Å, while on anatase, it bonds to two inequivalent Ti atoms, Ti5c and Ti6c, at distances of 2.34 Å and 2.50 Å, respectively. As a result of this asymmetry on reduced anatase, there are three main peaks in the Pt $d$–PDOS of anatase (101) near the valence band maximum (VBM) compared to two for Pt on reduced rutile, as shown in Figs. 3(c) and 3(d). The split peaks at $-1.6$ eV and $-1$ eV on anatase are associated with the interaction of Pt with Ti5c and Ti6c, respectively. As a result of the stronger interaction of Pt with Ti5c the split $d$–band is pushed down to lower energies and slightly increases the width of the Pt $d$–band.

So far, our calculations show that (i) Pt binds more strongly to both rutile and anatase reduced surfaces than to the stoichiometric ones, and (ii) Pt binds more strongly to anatase than to rutile on both types of surfaces. Since it is clear that the binding energies alone cannot explain (in a sense, contradict) our experimental observation, another factor must play an important role in the selective growth of Pt on TiO$_2$. The stronger binding of Pt to the reduced surfaces shows that oxygen vacancy plays the important role of a strong anchoring site for adsorption. The next logical step is, therefore, to investigate how easy it is to create these nucleation sites on rutile (110) versus anatase (101).

TABLE I: Calculated binding energies per atom (in eV) of Pt and Pt$_2$ on stoichiometric (S) and reduced (R) rutile (110) and anatase (101) surfaces.

|          | Rutile, S | Anatase, S | Rutile, R | Anatase, R |
|----------|-----------|------------|-----------|------------|
| Pt       | 2.21      | 2.87       | 3.59      | 5.05       |
| Pt$_2$   | $-$       | $-$        | 3.69      | 4.71       |

It is important to notice that all the analyses so far have been at a single atom level. Our experimental results, on the other hand, indicate that the average size of visible Pt particles is $\sim 1$ nm, which will be composed of a few Pt atoms. We therefore took our investigation one step further by examining the binding of Pt$_2$ dimers to the reduced rutile and anatase surfaces. The lowest energy atomic configurations of Pt$_2$ bound to V$_O^-$ on rutile...
(110) and anatase (101) are shown in Figs. 2(e) and 2(f), respectively. On rutile, Pt$_2$ configuration seems very much like a combination of the structures of single Pt atoms on reduced and stoichiometric surfaces, as one Pt is still at the substitutional site and the other at the hollow position with a Pt-Pt distance of 2.52 Å. On anatase, a similar configuration occurs with one Pt at the substitutional site and the other in hollow position with a Pt-Pt bond at 2.50 Å. The calculated BEs per atom (Table I), 3.69 eV for rutile and 4.71 eV for anatase, reveal two interesting results. First, due to the increase in the BE per atom from 3.59 eV to 3.69 eV, we conclude that a single oxygen vacancy on rutile (110) can bind two Pt atoms, in contrast to the instability of Au$_2$ on the same surface with respect to a single Au atom bound at $V_0$ site and a diffusing Au atom.[1] Second, although the BE per atom on anatase is still larger than that on rutile, BE/atom for Pt$_2$ on anatase has decreased by 0.34 eV compared to a single Pt atom, showing the instability of a Pt$_2$ cluster with respect to 2 separate Pt atoms anchored at far away oxygen vacancies. Although we do not necessarily expect that this trend will evolve monotonically as the number of Pt atoms in the cluster increases (it does not, for Au clusters[10]), the present results suggest that rutile (110) surface could trap larger Pt clusters at oxygen vacancy sites compared to anatase. Indeed, although it is for the anatase (001) surface, it has already been reported that upon heating in vacuum at between 300 and 670K, coalescence of Pt islands was observed on rutile (110), but not on anatase (001)-(1×4).[17]

In summary, we have performed a comparative first principles study of Pt and Pt$_2$ on reduced and stoichiometric rutile (110) and anatase (101) surfaces in order to address the microscopic origin of our recent experimental finding of preferential growth of Pt on rutile TiO$_2$ rather than anatase. Our results indicate that (i) Pt and Pt$_2$ bind more strongly to anatase surfaces compared to rutile, but oxygen vacancies as the preferred nucleation sites of Pt clusters will be significantly more abundant on rutile, and (ii) $V_0$ on rutile can bind a Pt$_2$ cluster, while on anatase, Pt$_2$ is found to be unstable with respect to two isolated Pt atoms anchored at $V_0$ sites. Therefore, we conclude that the selective growth of Pt on rutile must be controlled by the relative number of available nucleation sites ($V_0$) and the seemingly stronger tendency of $V_0$ on rutile to trap more Pt particles compared to anatase. Incorporation of larger Pt clusters and their diffusion are necessary to further improve our understanding of the possible phenomena behind the SMSI and the dense clustering of Pt on rutile. This work was supported by the ACS Petroleum Research Fund under grant #s 40028-AC5M and 37552-AC5, and by NCSA under grant # DMR030053.

[1] For an excellent review, see U. Diebold, Surf. Sci. Rep. 48, 53 (2003) and references therein.