Fe(II)Ti(IV)O₃ Mixed Oxide Monolayer at Rutile TiO₂(011): Structures and Reactivities

Zhan-Hui Wen¹, Sandamali Halpegamage,² Xue-Qing Gong^{1,*} and Matthias Batzill²

¹*Key Laboratory for Advanced Materials, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P.R. China*

²*Department of Physics, University of South Florida, Tampa, FL 33620, USA*

**Email: xgong@ecust.edu.cn*

ABSTRACT: Mixed-metal oxide monolayer grown at an oxide support is of great potential in applications like heterogeneous catalysis. In this work, the experimentally obtained ordered mixed FeTiO₃ oxide monolayer supported by rutile TiO₂(011) surface has been carefully studied with density functional theory calculations. The genetic algorithm based optimization scheme has been employed to improve the searching capacity for possible structures, and a well ordered mixed Fe(II)Ti(IV)O₃ monolayer oxide structure much more stable than the one proposed previously has been successfully located. The new surface structure consists of uniformly distributed Ti and Fe cations in the ratio of 2:1. The simulated Scanning Tunneling Microscopy image based on this model is well consistent with the experimental one. Our calculations have shown that the O vacancy formation energy is rather high at the surface. We have also studied the adsorption of O₂ and CO at the exposed Fe sites on the surface as well as their reactions. The adsorption energies of O₂ are generally higher than those of CO. The catalytic cycle of CO oxidation following an Eley-Rideal type mechanism has been located for CO to react with surface adsorbed O₂ and O.

Keywords: mixed oxide surface; density functional theory; O₂ adsorption; CO adsorption; CO oxidation; genetic algorithm

1. Introduction

Transition metal oxides are tremendously important in modern catalysis, largely owing to their unexpectedly high catalytic activities and unique redox properties [1-3]. They have a wide variety of technological applications in solar energy conversion, emission control and gas sensors [4-6]. As two key issues that can determine their performances in these applications, surface structures and

compositions of transition metal oxides have attracted intense interests. Moreover, in order to modify the catalytic properties of transition metal oxides, various approaches including doping with various other transition metals in the bulk or at surface have also been widely used, creating mixed-metal oxides whose structure and composition are even more complex. Accordingly, there has been a growing demand in studying the behavior of mixed-metal oxide catalysts [7-10], which have already been successfully applied in the areas such as selective hydrogenation, CO oxidation, NO reduction and photolysis of water [11-13].

For heterogeneous catalysts, metal nanoparticles are usually anchored at an oxide support, which has the main role to stabilize and disperse the metal particles. Unfortunately, to avoid lateral interactions as well as inhibit sintering of the supported nanoparticles, their concentrations are usually kept very low, which then reduces the number of catalytically active sites on the oxide support. Though the higher activity of metal nanoparticles with respect to their bulk phase is well-established, deposition of a metal oxide in monolayer (ML) or submonolayer amount over a second metal oxide host could create nanostructures which in turn enhance the concentrations of the active sites as well as the overall catalytic properties of the entire system. The first monolayer catalyst was reported in 1946, in which a monolayer of molybdena was obtained on the alumina support ($\text{MoO}_x/\text{Al}_2\text{O}_3$) [7]. In addition, the vanadia submonolayer or monolayer supported on metal oxides such as titania, ceria and alumina have also been known to be excellent catalysts in various applications including selective oxidation reactions [14-17]. Despite the fact that such supported vanadia submonolayer or monolayer exhibits higher catalytic activity and selectivity than the unsupported oxide, to determine its atomic structures still remains challenging [18,19]. A complicating factor to the determination is that different surface orientations of the metal oxide support can result in different dopant species and different physicochemical properties. In fact, the surface orientation of the metal-oxide support may be crucial for stabilizing catalytically active species. For instance, for catalytic combustion of methane over Pd/CeO_2 catalysts, the catalytically active phase was determined to be the mixed PdCeO_x surface layer on the specific $\text{CeO}_2(110)$ surface, which was formed under reaction conditions [20].

Titanium dioxide (TiO_2), in particular the rutile phase TiO_2 , is an important transition metal oxide with wide applications [21,22]. The lowest-energy rutile $\text{TiO}_2(110)$ has been very well understood, and it exhibits a bulk truncation structure with small surface relaxations. As the second most popular surface orientation, $\text{TiO}_2(011)$ has been found to exhibit a stronger activity toward oxidation reactions

than the $\text{TiO}_2(110)$ surface in photocatalysis, and it shows a complex surface reconstruction with (2×1) periodicity [23-26]. At the same time, iron as a dopant cation has been widely used and studied [27,28]. Interestingly, titanium dioxide and iron oxide could form various stable bulk mixed oxides, and specifically, ilmenite is the most prominent mineral and common source for titanium in the Earth's crust, which is composed as Fe(II)Ti(IV)O_3 . In addition, small amount of iron impurities in anatase or rutile TiO_2 have been reported previously to segregate to the surface by vacuum annealing, but no ordered mixed oxide layer at the surface was formed [29,30]. Very recently, we have reported an ordered Fe/Ti mixed oxide surface layer on the rutile $\text{TiO}_2(011)$ surface through combined experimental and computational studies [31], and a preliminary structural model based on the ilmenite surface has been proposed to describe the atomic configuration of the mixed oxide layer.

In this work, in order to fully exam the possible structures of the Fe/Ti mixed oxide surface layer formed at the rutile $\text{TiO}_2(011)$ support, we performed systematic density functional theory (DFT) calculations aided by genetic algorithm (GA) optimization. Various surface structures with unique and ordered atomic configurations have been obtained, and a structure with much higher stability and better consistency with experimental observations than that proposed previously was successfully determined. In addition, aiming at illustrating the potential application of such mixed oxide layer in catalysis, we also calculated the adsorptions of CO and O_2 molecules as well as their reactions.

2. Computational details

We used the genetic algorithm optimization method embedded in the Universal Structure Predictor Evolutionary Xtallography (USPEX) code to search for stable surface structures, which has been successfully applied for predicting stable structures of bulk crystal, nanoclusters, surface reconstruction, etc [32-35]. As a global optimization method, the USPEX code uses four ways, namely hereditary, mutation, transmutation, and random, to produce new surface structures.

The DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [36,37] with the generalized gradient approximation (GGA) [38] using the all-electron projector-augmented wave method. The titanium and iron 3s, 3p, 3d and 4s and the carbon and oxygen 2s and 2p electrons were treated as valence electrons. The valence electronic states were expanded in plane wave basis sets with an energy cutoff of 400 eV. The calculated lattice parameters of bulk rutile TiO_2 are $a=b=4.660 \text{ \AA}$, $c=2.973 \text{ \AA}$. For the determination of the mixed oxide layer structure, the

reconstructed $\text{TiO}_2(011)$ was modeled by a surface slab extended in a (2×1) supercell, and a Monkhorst-Pack grid of $(1 \times 2 \times 1)$ k-point mesh was used. The vacuum height was about 15 Å. In the structural optimization, we relaxed the atom positions in the surface and buffer region (top two layers), while the other atoms (bottom two layers) were fixed, and each candidate structure was relaxed until the residual forces were below 0.05 eV/Å. In the calculations of O_2 and CO adsorptions at the surface, as well as their reactions, the surface slab was modeled by a (2×2) supercell containing four TiO_2 layers and the topmost three layers and the adsorbed molecules were allowed to relax.

To estimate the adsorption energies, the following equation was used:

$$E_{\text{ads}} = -(E_{\text{A/Mixed}} - E_{\text{A}} - E_{\text{Mixed}})$$

where $E_{\text{A/Mixed}}$ is the total energy of the interacting system containing adsorbate A at the mixed $\text{Fe(II)Ti(IV)O}_3/\text{TiO}_2(011)$ surface ($\text{A} = \text{CO}, \text{O}_2$, etc.), and E_{A} and E_{Mixed} are energies of the gas-phase molecule and the $\text{Fe(II)Ti(IV)O}_3/\text{TiO}_2(011)$ surface slab with mixed oxide monolayer, respectively.

The transition states (TS) in reactions were located with a constrained optimization scheme [39] and were verified when all forces on atoms vanish and the total energy is a maximum along the reaction coordinate but a minimum with respect to the rest of the degrees of freedom.

In order to better compare the calculated surface structures, we have also simulated STM images within Tersoff–Hamann’s approach [40] in the constant height mode. An empty-state window of 1.2 eV above the edge of the conduction band was employed, and the simulated STM images were plotted at the height of 2 Å above the topmost atoms of the surfaces.

It needs to be mentioned that the GGA based DFT calculations may have drawbacks such as the tendency to underestimate the electronic band gap. However, in the current work, we mainly performed the calculations to compare the stabilities and STM patterns of different surface structures as well as the adsorption strengths of different molecules at the same site of the surface. We believe that the calculation results should be still largely reliable for such comparisons.

3. Results and discussion

3.1 USPEX optimization results

In this work, the complicated structures of the Fe(II)Ti(IV)O_3 mixed oxide monolayer supported on the $\text{TiO}_2(011)$ surface were systematically calculated with the genetic algorithm

aided total energy DFT calculations. In particular, the GA method was used for generating structures and helping us to obtain a large set of possible metastable and global minimum structures, which may even provide information on surface evolution. On the basis of the previous experimental measurement regarding the composition of the Fe-Ti mixed oxide monolayer, we constructed the surface by adding two FeO units in each 2×1 rutile $\text{TiO}_2(011)$ surface cell [31]. In other words, the Fe(II)Ti(IV)O_3 mixed oxide monolayer actually consists of $1/2$ ML of Fe(II)O oxide with respect to the exposed TiO_2 surface units on the original surface.

Fig. 1. Side view of various calculated structural models for $1/2$ ML FeO on a rutile $\text{TiO}_2(011)$ surface and simulated Scanning Tunneling Microscopy images. Ti atoms are in gray, O in red, and Fe in violet.

Table 1

Calculated relative energies of different surface structures with $1/2$ ML FeO on the rutile $\text{TiO}_2(011)$.

Structures	Fig. 1(a)	Fig. 1(b)	Fig. 1(c)	Fig. 1(d)	Fig. 1(e)	Fig. 1(f)
ΔE (eV)	-0.54	-0.02	-0.02	0	0.04	0.15

Through calculations, we obtained various stable structures of the Fe(II)Ti(IV)O_3 mixed oxide monolayer at $\text{TiO}_2(011)$, and the six structures with the lowest total energies are illustrated in Fig.

1(a-f). The relative total energies of these structures are listed in Table 1. Among these structures, the one illustrated in Fig. 1(d) is also the one reported in our previous work of the experimental measurement of this mixed oxide surface [31], which has obvious similarity with the ilmenite (012) surface. Interestingly, in the current work, by using improved optimization algorithm, we actually located several structures that are more stable, which even have no obvious ilmenite features. For the most stable mixed oxide surface layer (Fig. 1(a)), the Ti and Fe cations are uniformly distributed, very different from the previously reported one (Fig. 1(d)), in which the two FeO units actually form a dimer anchoring at the pristine $\text{TiO}_2(011)\text{-}1\times 1$ support. We also simulated and compared the Scanning Tunneling Microscopy (STM) images of the surface structures illustrated in Fig. 1(a) and Fig. 1(d) (see Fig. 1(g) and Fig. 1(h), respectively). As one can see from Fig. 1(g), the exposed Fe^{2+} at the most stable mixed oxide surface (Fig. 1(a)) give the brightest features in the simulated STM. Similarly, it can be seen from Fig. 1(h) that for the ilmenite-like mixed oxide surface (Fig. 1(d)), it is also the exposed Fe^{2+} cations that give the brightest features. Apparently, the experimental STM images which exhibit a $c(2\times 1)$ structure [31] can be better represented by the simulated results in Fig. 1(g). It should be noted that the simulated STM image (Fig. 1(g)) also shows that besides the very bright features from surface Fe^{2+} , the exposed O_{2c} also give less bright features. This may indicate that tip effects play an important role in imaging strongly corrugated structures, and more sophisticated STM simulations may need to be employed [41].

According to the experimental procedures that Fe was deposited in a low O_2 background pressure at room temperature on the $\text{TiO}_2(011)\text{-}2\times 1$ surface, one may note that the located structure shown in Fig. 1(b) can be taken as the initial structure for the formation of the mixed oxide structure. In this structure, the FeO units appear to sit at the valley part of the reconstructed $\text{TiO}_2(011)\text{-}2\times 1$ surface, while the rest part of the substrate still keeps the 2×1 conformation. It then needs to be emphasized that since the whole top layer TiO_2 and the added FeO were included in the mixed oxide structure search, and the only such mixed oxide surface with the substrate largely keeping the 2×1 reconstruction was still determined to be much less favorable than the most stable one, one may expect that the FeO deposition can remove the reconstruction of the clean $\text{TiO}_2(011)$ surface, similar to the case of adsorptions of various organic molecules [42].

For the other located structures illustrated in Fig. 1, they largely keep the characteristics of those in Fig. 1(a) and Fig. 1(b), except that the surface Fe and Ti cations may exchange their positions.

3.2 O Vacancies

In Figs. 2(a) and (b), we illustrate the detailed structures of the most stable mixed oxide surface determined in this work in side and top views. One can see that the exposed Ti cations are all 6-fold fully coordinated, while the exposed Fe cations are only 4-fold coordinated and exhibit obvious dangling bonds, which may give rise to unique chemical activities at such Fe sites. Moreover, as the mixed oxide monolayer surface also exposes the O_{2c} lattice oxygen, one may expect that such lattice oxygen could be involved in surface reactions. We then calculated the O vacancy formation energy by using the following equation: $\Delta E = E_{\text{Mixed-Ov}} + 1/2 E_{O_2} - E_{\text{Mixed}}$, where E_{Mixed} is the total energy of the mixed oxide slab, and $E_{\text{Mixed-Ov}}$ and E_{O_2} are energies of the surface slab with one O vacancy (Fig. 2(c)) and the gas-phase O_2 molecule, respectively. We obtained the O vacancy formation energy of as high as 3.36 eV. It then indicates that the lattice O_{2c} on the Fe(II)Ti(IV)O₃ mixed oxide monolayer are quite stable and may not be able to directly involve in reactions. Therefore, in the current work, we then studied the adsorptions of different adsorbates and their reactions. Specifically, adsorptions of CO and O_2 molecules, as well as the corresponding CO oxidation reactions were systematically calculated.

Fig. 2. Detailed structures of Fe(II)Ti(IV)O₃/TiO₂(011). (a) side view; (b) top view; (c) O vacancy (O_v) from top view. The characteristic surface atoms are specified.

3.3 CO Adsorption

CO adsorption at the Fe(II)Ti(IV)O₃ mixed oxide monolayer grown at rutile TiO₂(011) was calculated at surface Fe cations (see Fig. 3). According to our calculation results, CO was preferentially adsorbed with carbon heading toward the exposed Fe in an approximately perpendicular configuration with respect to the surface plane. The adsorption energies calculated with different coverages are listed in Table 2. In the case of the adsorption of a single CO in each 2×2 surface cell (coverage = 1/4 ML with respect to the number of Fe sites, Fig. 3(a)), the adsorption energy was calculated to be 0.85 eV. Under higher coverages, the adsorption energies of CO were calculated to be 0.88 eV (1/2 ML), 0.89

eV (3/4 ML) and 0.91 eV (1 ML) (see Figs. 3(b-c), respectively). These results indicate that there exist slightly favorable interactions among co-adsorbed CO at the Fe(II)Ti(IV)O₃ mixed oxide monolayer. It needs to be noted that the surface Ti cations of the mixed oxide monolayer were calculated to give rise to rather weak CO adsorption, in consistence with the fact that they are fully coordinated.

Fig. 3. Calculated structures (top view) of CO adsorptions at Fe(II)Ti(IV)O₃/TiO₂(011) surface under different coverages. C atoms are in dark grey and O of CO in green.

Table 2

Calculated (average) adsorption energies (in eV) of CO at Fe(II)Ti(IV)O₃/TiO₂(011) under different coverages.

Coverages	1/4 ML	1/2 ML	3/4 ML	1 ML
$E_{\text{ads}}(\text{CO})$	0.85	0.88	0.89	0.91
Fig.	3(a)	3(b)	3(c)	3(d)

3.4 O₂ Adsorption

The calculated adsorption structures of O₂ molecules in different configurations and under different coverages at Fe cations are illustrated in Fig. 4, and the calculated average adsorption energies are listed in Table 3. For the mixed oxide monolayer, the exposed Fe²⁺ can be further oxidized to Fe³⁺ by transferring one electron to the adsorbate. Accordingly, one may expect that O₂ can be favorably adsorbed at the exposed Fe on such Fe(II)Ti(IV)O₃ monolayer. From the calculated structures presented in Fig. 4, one can see that a single O₂ molecule in the surface cell (1/4 ML) can have two adsorption configurations, which give rise to the adsorption energies of 1.16 eV (Fig. 4(a)) and 0.99 eV (Fig. 4(b)), respectively. In Fig. 4(a), we show that the O₂ is adsorbed in bidentate configuration by forming two equivalent bonds (1.851 Å) with Fe, while in Fig. 4(b), we show that the O₂ only forms one O-Fe bond with Fe, and the bond length is 1.931 Å. Then we calculated the co-adsorption of two O₂ molecules with different configurations (1/2 ML, see Fig. 4(c-e)) on the surface. The adsorption energies were determined to be 1.10 eV, 0.97 eV and 0.92 eV, respectively. From these calculated structures and average adsorption energies, we can learn that both O₂ molecules prefer to take the bidentate

configuration to bind with exposed surface Fe. We also calculated the 3/4 ML and 1 ML coverages for O_2 molecules (not shown), and we found that when all the adsorbed O_2 take the bidentate configuration, the calculated average adsorption energies are 0.74 eV and 0.66 eV, respectively, which are significantly lower than those obtained at lower coverages. By contrast, the highest average O_2 adsorption energy (0.99 eV) for the 3/4 ML coverage was obtained when only one O_2 molecule binds with the exposed Fe in monodentate configuration, while the other two take the bidentate configuration. When 1 ML of adsorbed O_2 molecules occur on the Fe(II)Ti(IV) O_3 monolayer surface, the highest average adsorption energy was determined to be 0.94 eV, corresponding to the surface conditions that two O_2 molecules take the bidentate configuration. In general, as one can see from Table 3, with the increasing coverage of O_2 molecules on the Fe(II)Ti(IV) O_3 mixed oxide monolayer, the average adsorption energies of O_2 gradually decrease, indicating the existence of repulsive interactions among co-adsorbed O_2 molecules. Nevertheless, compared with CO, the adsorbed O_2 still have relatively higher adsorption energies, suggesting that the mixed oxide monolayer surface may have larger population of adsorbed O_2 .

Fig. 4. Calculated structures (side view) of O_2 adsorptions at Fe(II)Ti(IV) O_3 /Ti O_2 (011) surface under different coverages.

Table 3

Calculated (average) adsorption energies (in eV) of O₂ at Fe(II)Ti(IV)O₃/TiO₂(011) under different coverages.

Coverage	E _{ads}	E _{ads}	E _{ads}	E _{ads}	E _{ads}
1/4 ML	1.16	0.99			
	Fig. 4(a)	Fig. 4(b)			
1/2 ML	1.10	0.97	0.92		
	Fig. 4(c)	Fig. 4(d)	Fig. 4(e)		
3/4 ML	0.74	0.99	0.98	0.94	
	/	Fig. 4(f)	Fig. 4(g)	Fig. 4(h)	
1ML	0.66	0.85	0.94	0.93	0.93
	/	Fig. 4(i)	Fig. 4(j)	Fig. 4(k)	Fig. 4(l)

3.5 Co-adsorption of CO and O₂ at Fe(II)Ti(IV)O₃

According to the calculated adsorption energies reported in the above, the adsorption of O₂ molecules is energetically more favorable than that of CO at the exposed Fe of the Fe(II)Ti(IV)O₃ mixed oxide monolayer, and therefore, the surface would probably favor the adsorption of O₂. However, mixed adsorption domains containing both CO and O₂ may still occur as the average O₂ adsorption energies are very close to those of CO under high coverages (see Tables 2 and 3). So, in the current work, we still calculated the adsorption of CO after nO₂ (n=1~3 in each surface cell) molecules have been adsorbed on the surface. The calculated co-adsorption structures are presented in Fig. 5 and the corresponding optimized structures are illustrated in Table 4. Indeed, one can see from these results that co-adsorbed O₂ can significantly reduce the adsorption strength of CO, and only when the coverage of O₂ is rather low CO may still be able to adsorb with reasonable stability under mild conditions.

Fig. 5. Calculated structures (side view) of CO adsorption after nO₂ (n=1~3, a-c) molecules had been adsorbed at Fe(II)Ti(IV)O₃/TiO₂(011) surface.

Table 4

The calculated CO adsorption energies (in eV) at Fe(II)Ti(IV)O₃ with nO₂ (n=1~3).

Model	FeTiO ₃ -O ₂	FeTiO ₃ -2O ₂	FeTiO ₃ -3O ₂
E _{ads} (CO)	0.62	0.42	0.42

3.6 CO Oxidation

The active site, where the adsorption/activation of reactants and their subsequent reactions occur, is key to heterogeneous catalysis. Only after the nature of the active site is accurately determined, the reaction mechanism can be well understood, allowing for the rational design of new catalysts [43]. For the Fe(II)Ti(IV)O₃ mixed oxide monolayer, the exposed Fe can be taken as the active site for catalytic oxidation reactions since it appears to be the only site for adsorptions of molecules like CO and O₂. In the current work, catalytic CO oxidation was taken as the probe reaction to help understand the possible catalytic activities of the Fe(II)Ti(IV)O₃ mixed oxide monolayer. It needs to be mentioned that the for CO oxidation by oxygen molecule, it may follow the Langmuir-Hinshelwood or Eley-Rideal mechanism, in which CO reacts with adsorbed O₂ either following its own adsorption or by directly combining with adsorbed O₂ from gas phase. It should be noted that the reaction may also follow the Mars-van Krevelen (MvK) type catalytic cycle, in which adsorbed CO reacts with surface lattice O first, and O₂ then adsorbs and recovers the missing lattice O.

According to the calculation results of CO and O₂ adsorptions reported above, CO may not be able compete with O₂ for adsorption and therefore may not co-exist with O₂ on the surface. In fact, the distance between the nearest two exposed Fe is as long as 5.383 Å, suggesting that these two molecules would not be able to readily combine and react even if co-adsorption occurs. Moreover, the calculated O vacancy formation energy (3.36 eV) is quite high, suggesting that surface O would be inert and the MvK reaction cycle would not be feasible. Therefore, in the current work, we only considered the CO oxidation through its collision with O₂ sitting at the Fe(II)Ti(IV)O₃ mixed monolayer oxide surface from the gas phase. The calculated reaction pathway is plotted in Fig. 6. As the adsorbed O₂ has two adsorption configurations at Fe(II)Ti(IV)O₃ monolayer surface, in Fig. 6(a) and Fig. 6(b), we presented the CO oxidation reaction pathways with surface O₂ molecule in such bidentate and monodentate configurations, respectively. For the corresponding transition state, the OC-OO distance decreases to

1.642 Å in the pathway shown in Fig. 6(a), and the barrier was estimated to be 0.94 eV. CO₂ occurs as the result of the CO reaction with O₂ with very weak adsorption strength. On the other hand, the OC-OO distance decreases to 1.705 Å in the transition state of the reaction pathway shown in Fig. 6(b), and the barrier was estimated to be 0.61 eV. Again, CO₂ occurs as the result of the reaction of these two molecules with a neglectable adsorption energy. After the CO₂ desorbs, the surface is left with a single adsorbed O (O_{ad}) at the exposed Fe, which can be involved in the reaction with another CO. As presented in Fig. 6(c) this reaction pathway also occurs with the direct collision of the gas phase CO with O_{ad}. The OC-O_{ad} distance decreases to 1.834 Å in the transition state, and the barrier was estimated to be 0.36 eV. After CO₂ desorbs, this surface recovers the original state, indicating that a sustainable catalytic cycle for CO oxidation can be properly maintained.

Fig. 6. Calculated energy profiles of CO oxidation by adsorbed (a, b) O₂ and (c) single O_{ad} at the Fe(II)Ti(IV)O₃/TiO₂(011) surface. IS, TS and FS are the initial, transition and final states of the reactions, respectively.

4. Conclusion

In summary, by using the DFT calculations aided by genetic algorithm embedded in USPEX code, we extensively searched for stable surface structures of the mixed Fe(II)Ti(IV)O₃ surface oxide layer and found several structures more stable than the one reported previously. The most stable Fe(II)Ti(IV)O₃ mixed oxide surface structure is well consistent with the experimental one on the basis of the simulated STM images. Moreover, one less stable structure can be taken as the initial structure for the doping of FeO at reconstructed TiO₂(011)-2×1 surface. In order to understand the chemical

properties of the determined surface, we have studied the adsorption of CO and O₂ molecules on the most stable Fe(II)Ti(IV)O₃ mixed oxide surface and their reactions. The surface under-coordinated Fe cations were found to be the active sites. The average adsorption energies of O₂ are larger than those of CO under different coverages, and an Eley-Rideal type reaction mechanism has been located for gas-phase CO to readily react with pre-adsorbed O₂ at the mixed oxide surface.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21573067, 21421004, 21322307), “Shu Guang” project of Shanghai Municipal Education Commission and Shanghai Education Development Foundation (13SG30) and the Programme of Introducing Talents of Discipline to Universities (B16017). The authors also thank the computing time in the National Super Computing Center in Jinan. The USF group acknowledges support from the Department of Energy-Office of Basic Energy Sciences under DE-FG02-09ER1608 and the National Science Foundation under CHE-1505609.

References

- [1] L. Peng, T. Xie, Y. Lu, H. Fan, D. Wang, *Phys. Chem. Chem. Phys.* 12 (2010) 8033.
- [2] X. Sun, X. Cao, P. Hu, *Sci. Chi. Chem.* 58 (2015) 553.
- [3] H. Tada, Q. Jin, H. Nishijima, H. Yamamoto, M. Fujishima, S. Okuoka, T. Hattori, Y. Sumida, H. Kobayashi, *Angew. Chem. Int. Ed.* 50 (2011) 3501.
- [4] X. Mao, Z. Wang, X. Lang, Q. Hao, B. Wen, D. Dai, C. Zhou, L.-M. Liu, X. Yang, *J. Phys. Chem. C* 119 (2015) 6121.
- [5] Y.-Y. Yu, X.-Q. Gong, *ACS Catal.* 5 (2015) 2042.
- [6] C.L. Pang, R. Lindsay, G. Thornton, *Chem. Soc. Rev.* 37 (2008) 2328.
- [7] D.J. Stacchiola, S.D. Senanayake, P. Liu, J.A. Rodriguez, *Chem. Rev.* 113 (2013) 4373.
- [8] J.B. Park, J. Graciani, J. Evans, D. Stacchiola, S.D. Senanayake, L. Barrio, P. Liu J.F. Sanz, J. Hrbek, J.A. Rodriguez, *J. Am. Chem. Soc.* 132 (2010) 356.
- [9] V.I. Avdeev, V.M. Tapilin, *J. Phys. Chem. C* 114 (2010) 3609.
- [10] W.-J. An, W.-N. Wang, B. Ramalingam, S. Mukherjee, B. Daubayev, S. Gangopadhyay, P. Biswas, *Langmuir* 28 (2012) 7528.

- [11] S. Bonanni, K. Aït-Mansour, H. Brune, W. Harbich, *ACS Catal.* 1 (2011) 385.
- [12] G. Halasi, T. Bánsági, F. Solymosi, *J. Catal.* 325 (2015) 60.
- [13] W. Zhu, S. Xiao, D. Zhang, P. Liu, H. Zhou, W. Dai, F. Liu, H. Li, *Langmuir* 31 (2015) 10822.
- [14] S. Agnoli, M. Sambì, G. Granozzi, C. Castellarin-Cudia, S. Surnev, M.G. Ramsey, F.P. Nezer, *Surf. Sci.* 562 (2004) 150.
- [15] V. Shapovalov, H. Metiu, *J. Phys. Chem. C* 111 (2007) 14179.
- [16] M. Baron, H. Abbott, O. Bondarchuk, D. Stacchiola, A. Uhl, S. Shaikhutdinov, H.-J. Freund, C. Popa, M.V. Ganduglia-Pirovano, J. Sauer, *Angew. Chem. Int. Ed.* 48 (2009) 8006.
- [17] T. Garcia, W. Weng, B. Solsona, E. Carter, A.F. Carley, C.J. Kiely, S.H. Taylor, *Catal. Sci. Technol.* 1 (2011) 1367.
- [18] I. Muylaert, P.V.D. Voort, *Phys. Chem. Chem. Phys.* 11 (2009) 2826.
- [19] I.E. Wachs, *Catal. Today* 100 (2005) 79.
- [20] S. Colussi, A. Gayen, M.F. Camellone, M. Boaro, J. Llorca, S. Fabris, A. Trovarelli, *Angew. Chem. Int. Ed.* 48 (2009) 8481.
- [21] U. Diebold, *Surf. Sci. Rep.* 48 (2003) 53.
- [22] W. Zhang, Z. Li, B. Wang, J. Yang, *Int. J. Quantum Chem.* 113 (2013) 89.
- [23] J. Tao, M. Batzill, *J. Phys. Chem. Lett.* 1 (2010) 3200.
- [24] X. Torrelles, G. Cabailh, R. Lindsay, O. Bikondoa, J. Roy, J. Zegenhagen, G. Teobaldi, W.A. Hofer, G. Thornton, *Phys. Rev. Lett.* 101 (2008) 185501.
- [25] X.-Q. Gong, N. Khorshidi, A. Stierle, V. Vonk, C. Ellinger, H. Dosch, H. Cheng, A. Selloni, Y. He, O. Dulub, U. Diebold, *Surf. Sci.* 603 (2009) 138.
- [26] C.L. Pang, A. Yurtsever, J. Onoda, Y. Sugimoto, G. Thornton, *J. Phys. Chem. C* 118 (2014) 23168.
- [27] X.-S. Liu, X.-D. Wang, M. Yao, W. Cui, H. Yan, *Catal. Commun.* 63 (2015) 35.
- [28] A. Busiakiewicz, *Thin Solid Films* 550 (2014) 347.
- [29] A. Busiakiewicz, *Appl. Surf. Sci.* 311 (2014) 391.
- [30] M. Setvín, B. Daniel, V. Mansfeldova, L. Kavan, P. Scheiber, M. Fidler, M. Schmid, U. Diebold, *Surf. Sci.* 626 (2014) 61.
- [31] S. Halpegamage, P. Ding, X.-Q. Gong, M. Batzill, *ACS Nano* 9 (2015) 8627.
- [32] A.R. Oganov, C.W. Glass, *J. Chem. Phys.* 124 (2006) 244704.
- [33] A.R. Oganov, A.O. Lyakhov, M. Valle, *Acc. Chem. Res.* 44 (2011) 227.

- [34] Q. Zhu, L. Li, A.R. Oganov, P.B. Allen, Phys. Rev. B 87 (2013) 195317.
- [35] Q. Wang, A.R. Oganov, Q. Zhu, X.-F. Zhou, Phys. Rev. Lett. 113 (2014) 266101.
- [36] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
- [37] G. Kress, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [38] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [39] A. Alavi, P. Hu, T. Deutsch, P.L. Silvestrelli, J. Hutter, Phys. Rev. Lett. 80 (1998) 3650.
- [40] J. Tersoff, D. R. Hamann, Phys. Rev. B 31 (1985) 805.
- [41] T. Woolcot, G. Teobaldi, C.L. Pang, N.S. Beglitis, A.J. Fisher, W.A. Hofer, G. Thornton, Phys. Rev. Lett. 109 (2012) 156105.
- [42] Q. Cuan, J. Tao, X.-Q. Gong, M. Batzill, Phys. Rev. Lett. 108 (2012) 106105.
- [43] P. Jiang, X. Bao, M. Salmeron, Acc. Chem. Res. 48 (2015) 1524.