

Supplementary Information

DFT Modelling Study of Pt Layer on Catalyst supports of Titanium Oxide, Nitride and Carbide

W11S17: Computational Screening of Supported Metal Films

Xin Xia,^{a*}

*a North China Electric Power University,
No.2 Beinong Road, Beijing, China 102206*

Glenn Jones,^b

b Johnson Matthey Technology Centre, Pretoria

Misbah Sarwar,^c Qian Tang,^c Ian Harkness,^c David Thompsett^c

*c Johnson Matthey Technology Centre,
Blounts Court, Reading, Berkshire, UK RG4 9NH*

1. The models of MO₂ support:

The bulk structures of rutile MO₂ (M= Ti, Ru, Ir) were optimized based on the literature lattice parameters [27-32]. Relaxations were performed using 1x1x2 supercells with constant volume and unconstraint volume to achieve the equilibrium lattice structure. The DFT calculation results in **Table S1** suggest employing the RPBE functional could expand the lattice parameter by 2% compared to the experimental values. However, the c/a ratios remain in a reasonable agreement with experimental results. A significant lattice/bond relaxation can be observed for the calculations of bulk structures using RPBE functional which is developed to correct the overbinding effect of DFT for chemisorption study. [43] Other than the exchange-correlation functionals, the supercell size also has a noticeable influence on the structure relaxation. The RPBE calculations show TiO₂ to be an insulator and RuO₂ and IrO₂ to be conductive. The calculated band gap of R-TiO₂ (2.01eV) is about 30% below the experimental value of 3.06 eV. This is a well-known limitation of DFT, which underestimates band gaps due to the insufficient cancellation of the self-interaction

correction inherent in the local exchange functional schemes. By using a Hubbard corrected DFT+U functional ($U=6\text{eV}$), the band gap of rutile TiO_2 can correctly predicted, however, this U value is not transformable for the study of other oxide structures.

Table S1 Calculation results of rutile structure MO_2 ($M= \text{Ti, Ru, Ir}$)

Rutile Structure	Methods	a(Å)	c/a	u
TiO₂	RPBE	4.701	0.634	0.306
	PBE ^[33]	4.639 ^a	0.64 ^a	0.305 ^a
	PW91	4.652	0.638	0.304
	LDA ^[33]	4.563 ^a 4.564	0.644 ^a 0.642	0.304 ^a 0.304
	Exp. ^[27-29]	4.594	0.644	0.305
RuO₂	RPBE	4.561	0.680	0.305
	PBE ^[33]	4.534 ^c	0.683 ^c	0.305 ^c
	PW91	4.526	0.688	0.305
	LDA ^[33]	4.440 ^c	0.693 ^c	0.306 ^c
	Exp. ^{[30][31]}	4.498 ^d	0.69 ^d	0.305 ^d
IrO₂	RPBE	4.680	0.695	0.308
	GGA	4.543	0.694	0.307
	LDA	4.492	0.692	0.308
	Exp. ^{[31][32]}	4.505	0.701	0.308

The surface stability of rutile MO_2 ($M= \text{Ti, Ru, Ir}$) has been studied. The low index surfaces (110), (100) and (001) have been modelled using the slab model. The calculation results suggest that the oxygen terminated (110) surfaces are the most stable, as indicated by the lower energies.

The R- TiO_2 (110) surface is modelled using periodic slabs consisting of several repeat units built of the $\text{O-Ti}_2\text{O}_2\text{-O}$ trilayers, separated by a vacuum gap of 25 Å. Each repeat unit is charge neutral and has a zero dipole moment in the direction normal to the surface. The oxygen terminated surfaces are calculated to be energetically favourable. The surface energy convergence with respect to the thickness of the slab model has been tested for TiO_2 (110), which shows an oscillating value of surface energy. This is considered to be due to the effect of the nonequivalence of the relaxed odd and even layer slabs. To overcome the difficulty of the energy oscillating with the thickness of surface slab, Harris and Quong^{[44][45]} suggest a 25% rule which allows

one to estimate the asymptotic surface energy from the average shift. According to their previous work, the converged energy values lie at 25% of the way between the three- and four-layer values. In this study, the surface energies of 3 and 4 trilayer surface slabs are calculated to be 0.84 and 0.58 J/m², respectively. The result of the 4 trilayer slab is in accordance with the experimental value of 0.58 J/m². Therefore, we decide to use the surface slab of 4 trilayer thickness for MO₂ (110) in subsequent study.

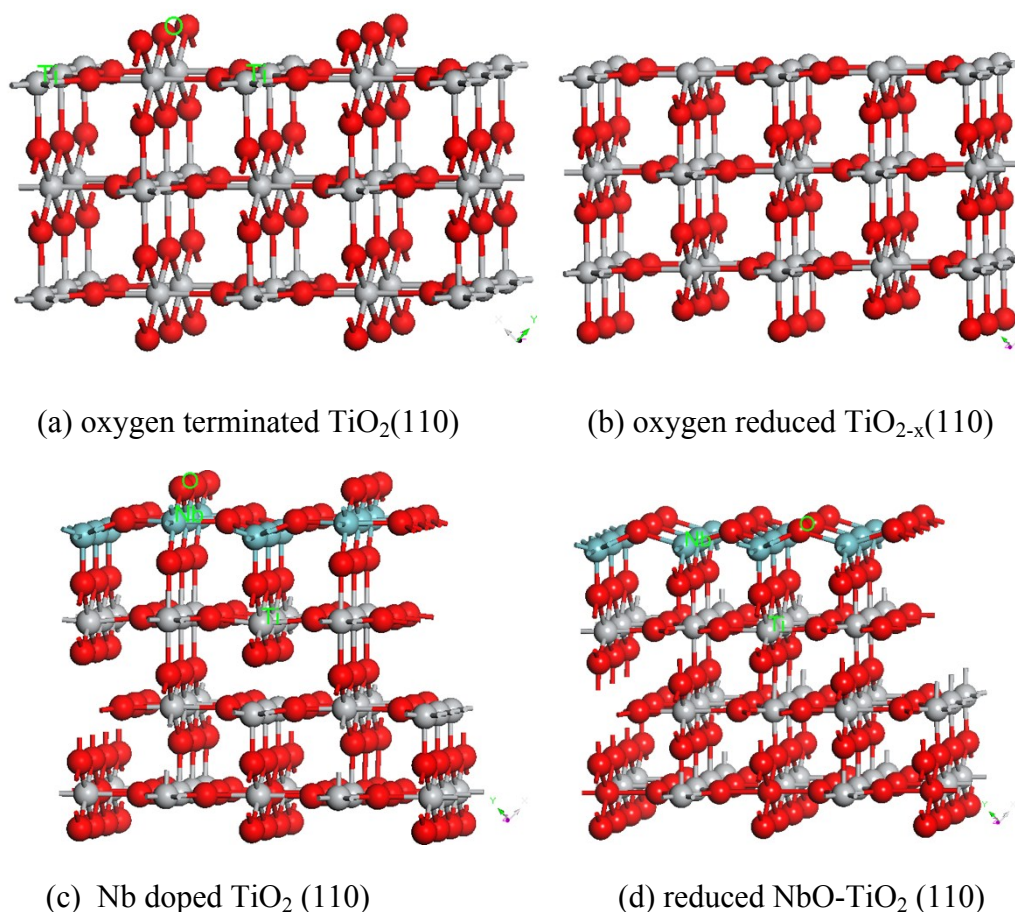


Figure S1. Surface structure models of (a) oxygen terminated TiO₂ (110), (b) oxygen reduced TiO_{2-x} (110), (c) Nb doped TiO₂ (110) and (d) reduced NbO-TiO₂ (110) surface. (O in red; Ti in grey; Nb in light blue)

In order to understand the effect of different cleavage surface planes on Pt wetting, the TiO₂ (100) was modelled to compare with TiO₂ (110). Based on the rutile TiO₂ (110) structure, an oxygen reduced form of TiO_{2-x}(110)^[12-15] surface was also created as well as a Nb-doped TiO₂(110) surface. It is suggested in the literature that Nb segregates to the surface of TiO₂ to form an NbO_x tie layer. ^[16] In our study, the reduced niobium oxides, both NbO₂ and NbO were considered and compared as the

tie layer (an interface between Pt and substrate support.) These models of rutile TiO_2 (110) related structures are shown in **Figure S1**.

The perovskite structure SrTiO_3 is also of interest since it can be viewed as an intercalated structure of six folded TiO_3 octahedral with Sr at the interstitial sites. The most stable surface of SrTiO_3 (100) and its possible surface terminations have been investigated by the modelling study. Both Sr-O and TiO terminated surfaces were considered.

The anatase TiO_2 structure have been modelled to compare with the rutile structure. The low index surface of A- $\text{TiO}_2(001)$, which contains fivefold Ti_{5c} as in the reduced R- $\text{TiO}_2(110)$ has been chosen for the Pt deposition study. The (001) surface of anatase titania is also the surface most often considered for catalytic applications. ^[46]

2. The calculation of segregation energy

An example of the Pt overlayer and underlayer model on rutile TiO_2 (110) has been illustrated in **Figure S2**. When moving the Pt overlayer to the underlayer, the entire TiO_2 trilayer is lifted up to accommodate the Pt atoms resulting in an energy increase of 0.9eV. Both of the full ML coverage structures I and II are much more stable than the over+underlayer model. Moving $\frac{1}{2}$ ML Pt in the overlayer structure to the subsurface interstitial site of TiO_2 (110) (i.e. structure III) requires an energy cost of 4.1eV. Therefore, the Pt skin is energetically favourable on the TiO_2 (110) support.

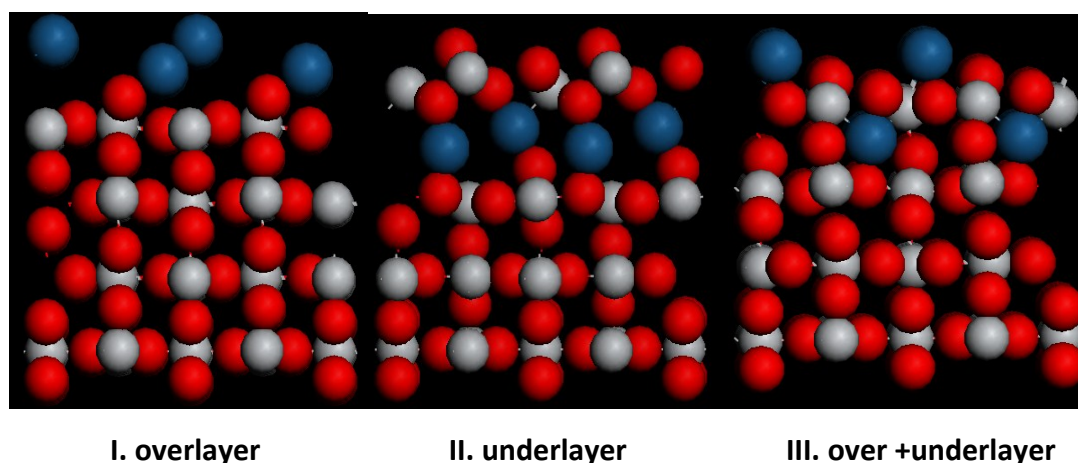


Figure S2. The Pt overlayer (I), underlayer (II) and mixed surface (over and underlayer) (III) on the support of rutile (110) oxides. (Pt in blue; Ti in grey; oxygen in red)

3. Pt stacking order on TiO₂ (110) and (100)

The stacking order for Pt deposition was modelled by adding Pt atom by atom on a surface unit of support structure. Due to the diversified geometry of support surfaces, the number of Pt atoms consists an overlayer plane are different. However, the stacking order study of Pt atoms were still limited by a relatively small surface cell. In order to check the relaxation effect of the Pt films, the obtained structure of 1ML Pt above the substrate surface have been tested by enlarging the surface unit to a supercell, e.g. 2x1 in the case of TiO₂(110) substrate, and 2x2 for TiO₂(001). The results suggest the stacking order of Pt overlayers remain the same, and the formation energy only has been reduced slightly.

Figure S3. Adding Pt atoms above R-TiO₂ (110) surface. n is the number of Pt atoms on a substrate surface unit. Considering the geometry of R-TiO₂ (110), three Pt atoms consist an Pt overlayer plane, i.e. n=3 N.

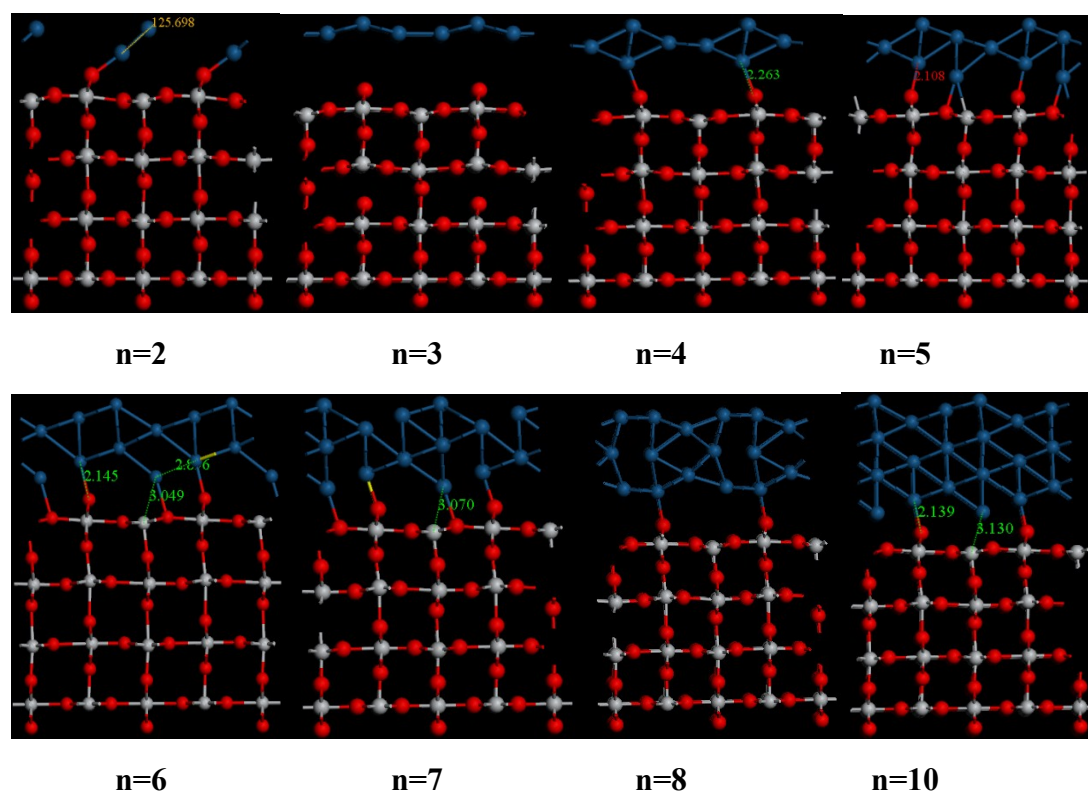
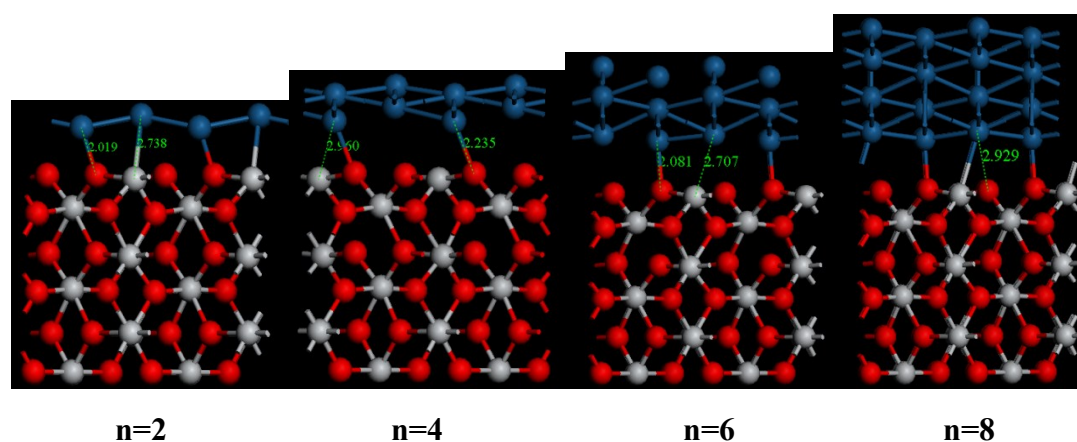


Table S2. Adding Pt atoms above TiO₂ (110) surface.

TiO ₂ (110)	n=1	2	3	4	5	6	7	8	9	10
E _{coh} eV	-22.36	-20.63	-19.29	-18.14	-17.14	-16.29	-15.55	-14.95	-14.40	-13.91
d(Pt-O) Å	2.09	2.21	4.22	2.26	2.11	2.15	2.15	2.10 2.25	2.16	2.14
d(Pt-Ti) Å	2.79	2.97	5.21	3.70	2.96	3.05	3.07	2.92	3.13	3.13

As shown in **Figure S3**, the bridging oxygen on the TiO₂ (110) surface is the active site to adsorb the 1st Pt atom. The 2nd Pt tends to bond with the 1st Pt rather than the lower surface sites oxygen or Ti. The 3rd and 4th Pt atoms stack on top of the surface oxygen. Starting from the 5th Pt, the close packed (211) surface of Pt has been formed. This stacking order would hold for more than 6 Pt atoms or 3 atomic layer of Pt deposition. However, the Pt-Pt bonds along the surface direction have been stretched by ≈ 0.2 Å. This is thought to be due to the fact that the surface area of the Pt (211) is slightly smaller than that of TiO₂ (110).

Figure S4. Adding Pt atoms above TiO₂ (110) surface. n is the number of Pt atoms on a substrate surface unit. On the R-TiO₂ (001) substrate, four Pt atoms consist an Pt overlayer plane, i.e. n=4N.**Table S3.** Adding Pt atoms above TiO₂ (001) surface.

TiO ₂ (001)	Pt=2	4	6	8	10
Ecoh eV	-19.14	-16.40	-14.55	-13.26	-12.31
d(Pt-O) Å	2.01	2.24	2.08	2.08	2.11
d(Pt-Ti) Å	2.73	2.96	2.70	2.76	2.93

A distorted Pt(111) surface has been found for Pt deposition above the TiO₂ (001) substrate. Half of the Pt(111) layer is lifted up by the surface Ti atoms since the Ti-Pt bond is longer than the Pt-O bond.

The energetics of Pt deposition on the TiO₂ surfaces are summarised in **Figure S5**

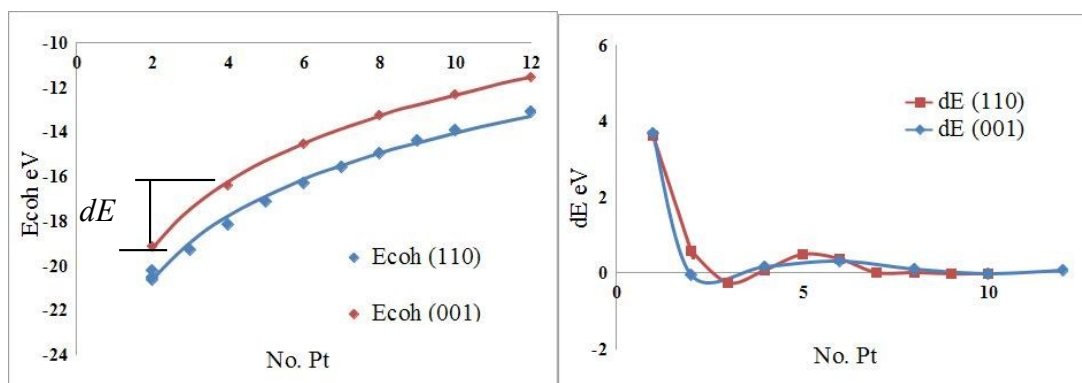


Figure S5 Pt growth on the support surfaces of TiO₂ (110) and (001). Left: The cohesive energy of Pt-TiO₂ system as a function of the number of Pt. Right: the binding energy increment, i.e. the energy requires for each Pt layer adding as a function of number of Pt atoms.

4. The DOS analysis of Pt atoms on TiO₂ (110) surface

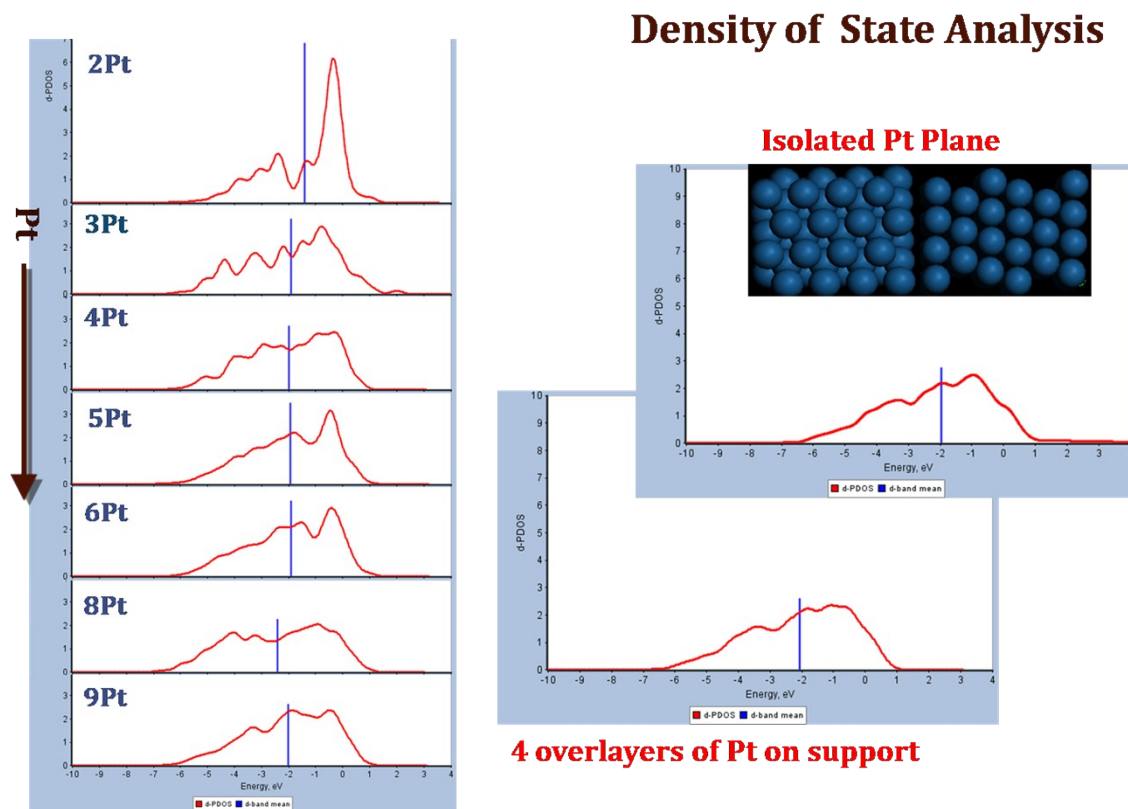


Figure S6 the density of state of Pt overlayer on TiO₂ (110) support.

5. Charge Analysis of TiX_n supports

Table S2 Pt-support TiX_n interfacial bond formation and Mulliken charge transfer. (Pt^{Ti} denotes the Pt atoms which forms bond with the Ti cations on the support surface. Pt^X denotes the Pt atoms bonding with surface anion X(X=O, N, C))

Supports TiX	d(Pt-Ti) Å	d(Pt-O/N,C) Å	Charge e Ti→Pt ^{Ti}	Charge e X→Pt ^X	E _{bind} [1 st Pt] eV
A-TiO ₂ (001)	2.49	1.97	-0.22	0.16 (Pt→O)	2.92
R-TiO ₂ (110)	2.97	2.21	-0.06	0.01	3.63
R-Ti _n O _{2n-2} (110)	2.71	2.83	-0.40	0.21	-0.12
TiO(100)	2.62		-0.47	0.05	<u>-1.42</u>
TiN(100)	3.44	2.39	-0.17	0.08	0.66
TiC(100)	2.93	2.01	0.09	-0.16 (C→Pt)	0.26