Supplementary Information

Exploring novel catalyst support materials in fuel cell application with DFT Modelling

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I. Support structures: bulk, surfaces and surface terminations

Metal oxides:

1) Rutile oxides MO_2 and the related structures

The bulk structures of rutile MO_2 (M= Ti, Ru, Ir) were reproduced based on the literature lattice parameters. [1][2] The most stable oxygen terminated MO_2 (110) surface has been modelled using a periodic slab consisting of several repeat units built of the $O–M_2O_2–O$

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. To overcome the difficulty of the energy oscillating with the thickness of surface slab, a 4 trilayer thickness for MO_2 (110) slab has been employed in the subsequent study.

2) Other oxide structures

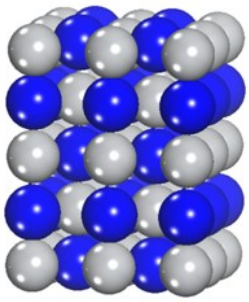
TiO_2 has several modifications, in addition to rutile, the anatase structure TiO_2 can also occur naturally. The anatase structure of TiO_2 also has been modelled by DFT study. The low index surface of anatase, TiO_2(001), has been employed for the modelling of the Pt ALD. The rock salt structure titanium oxide TiO[3] has been modelled to provide a data series of TiX (X= O, N, C) surfaces. SrTiO3 which has the perovskite structure 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. Moreover, the quartz structure SiO_2 [4] and the most stable SiO_2 (001) have also been modelled to give a comparison with SiC in later calculations of non-oxide supports.

Non-oxide supports:

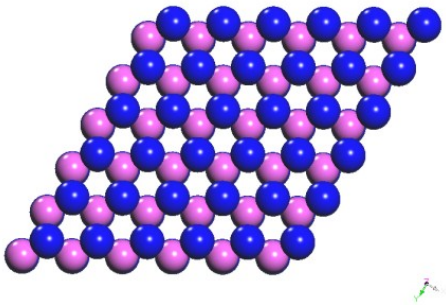
1) Nitrides

The transition metal nitrides, TiN and AlN have been studied as candidates for Pt support material since they have both good corrosion resistance and high electronic conductivity. TiN has a rock salt structure, however, this is not exactly stoichiometric. TiN compounds with a N/Ti ratio from 0.6 to 1.2[5] are thermodynamically stable, similar to TiO, which occurs in a range $TiO_{0.7}$ to $TiO_{1.3}$. [6] In this work, only the most energetically favourable surface of TiX(100) has been considered.

The wuritize structure AlN has been modelled. Different terminations of AlN(001) have been considered to produce the most stable support structure.



(a) TiN(100) side view



(b) AlN(100) top view

Figure S1 Nitride structure models of (a) TiN(100) (b) AlN(100). (Ti in grey, N in blue, Al in pink)

2) Carbides

Carbide supports of TiC, SiC, WC have also been modelled as candidate Pt support materials. The study of rock salt TiC gives a comparison with TiN and TiO. The calculated structures of TiX ((X= O, N, C) only show small differences in their lattice parameters. SiC is considered as an alternative support to carbon graphite which has the same lattice array and may enhance the Pt wetting through Si-Pt alloy formation. The wurtzite structure WC has been extensively discussed in the literature as a way of improving catalytic activity.

In the surface study of SiC and WC, different surface terminations need to be considered since the surface termination has a significant influence on the interfacial bond formation. For SiC(111) and WC(111), the C terminated surfaces are slightly more stable than the metal terminated surfaces.

In addition, some metal supports with good environmental resistance have also been included in the study. The bulk and surface structures of Ta and W have been modelled. The calculated surface energy of Ta and W are relatively high, which indicate that achieving a large surface area of this material may be difficult.

The structural and energetic results from DFT calculation are summarized in **Table S1**.

Table S1. Calculation results of support surfaces.

Structure	Surface	Surface area ($Å^2$)	Ecoh Per unit cell (eV)	Surface Energy J/m^2
Rutile	TiO_2 (110)	20.04	-8.30	0.58
	TiO_{2-X} (110)	20.04	-8.18	-
	Nb/TiO_2 (110)	20.04	-25.28	-
	TiO_2 (001)	22.64	-8.09	1.77
	RuO_2(110)	20.33	-7.08	0.90
	IrO_2(110)	21.57	-6.56	1.34
	SiO_2(110)*	16.15	-7.34	1.33
Anatase	TiO_2(001)	25.56	-24.59	1.31
Perovskite	$SrTiO_3$(100)	15.83	-7.44	0.88
Diamond	Si(111)	13.01	-4.86	1.51
	SiC(111) C terminated	8.30	-13.90	3.71
BCC metal	Ta(110)	8.01	-8.74	2.25
	W(110)	7.20	-10.75	3.08
Rock salt	TiO(100)	9.31	-15.53	0.57
	TiN (100)	9.11	-17.54	1.15
	TiC(100)	9.47	-16.67	1.45
Wuritize	AlN(100)	15.67	-13.78	2.13
	AlN(001)	8.46	-13.71	3.59
	WC(111) C terminated	7.42	-19.47	4.48

*SiO_2(110) is not included in further study of overlayer growth since no bond formation is observed between Pt and support substrate.

2. The stacking orders of three Pt surfaces

Table S2 lists the equilibrium structure of the three most stable Pt surfaces from theoretical calculations. The corresponding structures are shown as below.

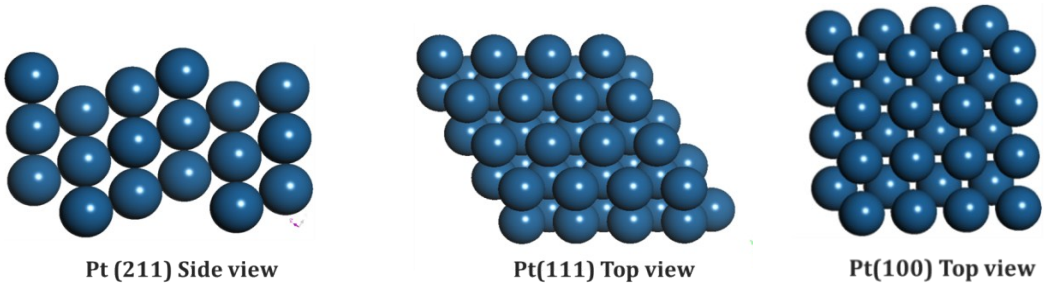


Figure S2 the (211), (111) and (100) surface of Pt.

Table S2 The structural and energetic results of the three most stable Pt surfaces (unsupported) from DFT calculations.

Surfaces	**Slab layer N**	**Lattice parameter(Å)**	**Surface occupation per Pt atom(Å²)**	**Surface Energy J/cm²**	**d band centre**
Pt(111)	4	a=b=5.669 (120°)	6.96 (27.84 unit cell)	1.37	2.17
Pt (100)	4	a=b=2.835 (90°)	8.04	1.57	1.86
Pt(211)	4	a=2.835 b=6.945 (90°)	6.56 (19.69 unit cell)	1.66	2.33(step) 2.01(top)

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