First principles modeling of composites involving TiO_2 clusters supported on M_2C MXenes†

Masoomeh Keyhanian,[a#] Néstor García-Romeral,[b#] Ángel Morales-García,[b*] Francesc Viñes,[b] Francesc Illas[b]

[a]*Department of Physical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar 47416-95447, Iran.*

[b]*Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1-11, 08028 Barcelona, Spain.*

[*]e-mail: angel.morales@ub.edu

[#]*Equally contributed*

Contents

Table S1. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Ti_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Ti_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-15.56	-33.66	0.85	17.24	-5.15
10	**-16.76**	**-36.95**	**2.21**	**17.98**	**-6.02**
20	-15.79	-34.11	1.78	16.55	-6.09
30	-13.66	-27.14	1.36	12.11	-4.69
40	-16.60	-27.61	0.67	10.34	-5.18
50	-16.60	-27.60	0.67	10.34	-5.19
60	-16.60	-27.63	0.68	10.35	-5.19
70	-14.85	-27.66	1.17	11.64	-5.17
80	-13.20	-25.36	1.15	11.02	-4.49
90	-13.02	-27.33	1.30	13.00	-4.79
100	-14.87	-31.91	0.90	16.14	-5.72
110	-14.87	-31.91	0.91	16.13	-5.71
120	-16.11	-34.56	0.93	17.52	-5.81
130	-14.86	-31.88	0.91	16.10	-5.72
140	-15.80	-32.84	0.91	16.13	-5.89

Table S2. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Zr_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Zr_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-10.42	-17.09	0.50	6.17	-3.71
10	-11.33	-18.94	0.82	6.79	-4.18
20	-13.09	-29.43	1.10	15.24	-5.44
30	-13.08	-29.43	1.11	15.24	-5.43
40	-12.87	-28.46	1.29	14.30	-5.39
50	-14.81	-26.90	0.75	11.33	-5.25
60	**-16.78**	**-36.03**	**1.06**	**18.19**	**-6.08**
70	-14.40	-30.23	0.77	15.06	-5.44
80	-14.40	-30.24	0.77	15.07	-5.45
90	-13.16	-27.24	1.12	12.96	-5.16
100	-13.15	-28.38	1.06	14.16	-5.39
110	-16.34	-34.71	0.98	17.38	-5.76
120	-14.80	-33.79	0.83	18.16	-5.60
130	-16.34	-34.69	0.98	17.37	-5.76
140	-13.15	-28.37	1.07	14.15	-5.39

Table S3. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Hf_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Hf_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-15.09	-34.50	0.75	9.38	-6.55
10	-11.97	-30.28	1.21	18.19	-5.25
20	-11.81	-26.58	0.90	17.41	-5.12
30	-14.80	-27.67	0.97	13.80	-5.82
40	-13.06	-25.54	0.59	12.27	-5.16
50	-16.99	-37.06	0.52	11.97	-6.61
60	**-16.99**	**-37.06**	**0.89**	**19.18**	**-6.62**
70	-16.99	-37.07	0.89	19.18	-6.63
80	-11.46	-24.52	0.89	19.20	-4.93
90	-12.40	-27.99	1.11	11.95	-5.27
100	-12.42	-29.85	0.84	14.75	-5.53
110	-14.97	-34.84	0.73	16.70	-6.04
120	-12.83	-29.66	0.71	19.16	-5.52
130	-12.40	-27.97	0.68	16.16	-5.26
140	-15.09	-34.50	0.84	14.73	-6.55

Table S4. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ V_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} V_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-11.20	-20.22	0.89	8.12	-3.28
10	-12.67	-25.47	1.43	11.37	-3.75
20	-12.55	-30.30	1.73	16.02	-4.78
30	-11.82	-24.09	1.32	10.95	-4.20
40	-12.28	-25.20	2.09	10.83	-4.04
50	-10.78	-19.70	1.46	7.45	-3.57
60	-12.65	-28.57	1.07	14.85	-4.37
70	-11.25	-20.37	1.11	8.01	-3.61
80	-12.33	-24.39	1.01	11.05	-3.79
90	-11.33	-19.06	0.74	6.98	-3.57
100	-13.37	-29.28	1.27	14.64	-4.64
110	-12.41	-27.27	1.08	13.78	-4.36
120	**-13.47**	**-27.89**	**0.71**	**13.71**	**-4.15**
130	-12.90	-26.40	1.22	12.29	-4.23
140	-13.37	-29.27	1.26	14.63	-4.64

Table S5. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Nb_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Nb_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-10.42	-15.35	0.74	4.19	-2.74
10	-12.11	-19.62	0.83	6.68	-3.12
20	-9.51	-20.28	1.27	9.50	-3.52
30	-9.51	-20.30	1.27	9.52	-3.53
40	-11.62	-24.93	1.09	12.23	-3.71
50	-10.90	-21.94	1.03	10.01	-3.38
60	-11.73	-22.29	1.18	9.38	-3.71
70	-10.91	-19.29	0.97	7.40	-3.51
80	-12.12	-19.39	0.78	6.48	-3.39
90	-10.12	-19.80	0.88	8.81	-3.44
100	-10.88	-27.35	1.76	14.71	-4.42
110	-11.81	-23.91	0.87	11.23	-3.78
120	**-13.08**	**-23.48**	**0.91**	**9.49**	**-3.53**
130	-11.81	-23.91	0.87	11.24	-3.79
140	-10.88	-27.33	1.76	14.69	-4.42

Table S6. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Ta_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Ta_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-11.68	-20.68	1.30	7.70	-2.88
10	-13.09	-21.50	1.11	7.30	-3.20
20	-12.99	-26.30	1.07	12.24	-3.62
30	-11.00	-25.83	1.26	13.57	-3.47
40	-11.05	-24.90	1.72	12.13	-3.90
50	-13.39	-27.12	1.19	12.54	-3.54
60	-13.05	-21.48	1.22	7.21	-3.36
70	-13.04	-21.52	1.22	7.25	-3.38
80	-13.04	-20.98	1.03	6.91	-3.44
90	-11.66	-21.12	1.29	8.18	-3.64
100	-10.95	-18.98	1.31	6.72	-2.97
110	-13.09	-21.49	1.12	7.29	-3.29
120	**-14.11**	**-25.40**	**1.09**	**10.19**	**-3.66**
130	-13.09	-21.47	1.11	7.27	-3.30
140	-10.95	-18.97	1.31	6.72	-2.97

Table S7. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Cr_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Cr_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-11.02	-22.01	2.54	8.44	-2.85
10	-11.02	-22.04	2.54	8.47	-2.84
20	-10.70	-22.68	1.95	10.02	-3.13
30	-9.83	-20.10	1.47	8.81	-2.94
40	-7.57	-12.90	1.10	4.23	-2.11
50	-10.32	-17.58	1.31	5.96	-2.48
60	-11.18	-21.83	1.80	8.86	-2.94
70	-10.47	-18.34	1.74	6.13	-2.58
80	-7.21	-11.66	1.17	3.28	-1.83
90	**-12.59**	**-24.95**	**1.57**	**10.79**	**-3.48**
100	-10.04	-19.53	1.40	8.09	-2.96
110	-10.39	-18.21	1.15	6.67	-2.63
120	-11.58	-21.78	1.34	8.86	-2.96
130	-11.88	-20.33	1.30	7.15	-2.63
140	-9.48	-15.70	1.03	5.19	-2.48

Table S8. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ Mo_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} Mo_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-8.79	-12.76	0.67	3.31	-1.89
10	-8.78	-12.77	0.66	3.34	-1.87
20	-9.58	-15.81	0.76	5.48	-2.16
30	-6.56	-11.62	0.64	4.42	-1.78
40	-8.81	-19.57	1.15	9.61	-2.25
50	-9.83	-17.27	0.89	6.55	-2.24
60	-10.03	-16.61	0.72	5.87	-2.17
70	-10.03	-16.61	0.71	5.86	-2.20
80	-9.97	-16.64	0.67	6.00	-2.24
90	-8.33	-14.48	0.72	5.43	-1.96
100	-8.12	-15.07	0.73	6.22	-2.13
110	**-10.12**	**-18.52**	**1.03**	**7.37**	**-2.34**
120	-9.64	-18.87	0.83	8.41	-2.46
130	-10.11	-18.53	1.03	7.38	-2.35
140	-8.13	-14.26	0.76	5.38	-2.08

Table S9. PBE calculated results for $(TiO_2)_5$ cluster at the $p(5\times5)$ W_2C (0001) surface with an α degree angle including adsorption, adhesion, and deformation energies (all in eV), which are labeled as E_{ads}, E_{adh}, and E_{def}, respectively. Note two different sets of data for the formation of the (0001) Ti_2C MXene surface and the $(TiO_2)_5$ cluster. These energies are calculated following Eqs. 1-3 of the main text. Charge transfer of $(TiO_2)_5$, ΔQ, given in *e*. The highlighted row corresponds to the most stable configuration.

α	E_{ads}	E_{adh}	E_{def} W_2C	E_{def} $(TiO_2)_5$	ΔQ
0	-9.54	-15.21	1.60	4.07	-1.97
10	-9.54	-15.21	1.60	4.07	-1.98
20	-9.05	-14.63	1.41	4.17	-1.67
30	-9.88	-21.55	1.10	10.57	-2.14
40	-8.28	-20.99	2.30	10.41	-2.16
50	-8.44	-14.97	1.47	5.06	-1.98
60	-8.82	-14.14	1.36	3.96	-1.93
70	-9.81	-16.87	1.51	5.56	-1.97
80	-9.81	-16.86	1.51	5.54	-1.98
90	-10.06	-19.65	1.76	7.84	-2.18
100	-8.37	-14.30	1.84	4.09	-2.17
110	**-10.37**	**-17.62**	**1.76**	**5.49**	**-2.04**
120	-9.56	-15.29	1.58	4.14	-1.96
130	-10.31	-17.69	1.80	5.58	-2.06
140	-10.31	-17.69	1.79	5.58	-2.04

Table S10. The *d*-band center values, ε_d, for the studied M_2C (0001) surfaces.[a]

Ti_2C	V_2C	Cr_2C
4.06	2.54	-0.72
Zr_2C	Nb_2C	Mo_2C
3.47	0.32	-0.72
Hf_2C	Ta_2C	W_2C
3.74	1.88	0.91

[a] R. Morales-Salvador, J. D. Gouveia, Á. Morales-García, F. Vines, J. R. Gomes and F. Illas, *ACS Catalysis*, 2021, **11**, 11248-11255.

Table S11. Electronegativities, χ_M, of the transition metal atoms in M_2C (0001) surfaces.[a]

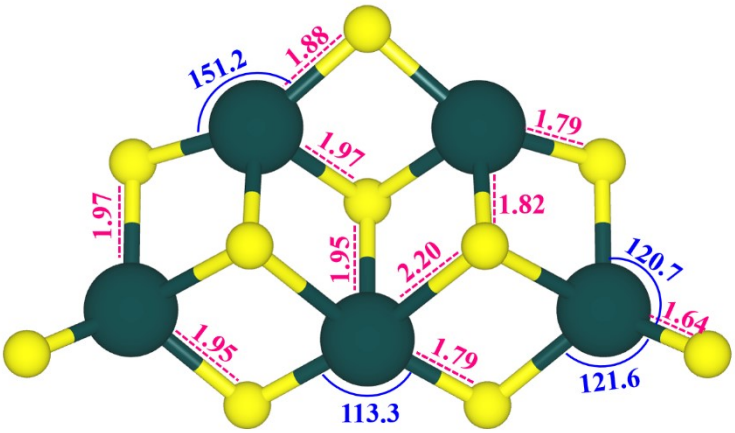
Ti	V	Cr
1.54	1.63	1.66
Zr	Nb	Mo
1.33	1.60	2.16
Hf	Ta	W
1.30	1.50	2.36

[a] John Emsley, The Elements, 3rd Edition. Oxford; Clarendon Press, 1998.

Table S12. The linear regression $y = a + bx$ parameters and R regression coefficients of trends reported in Figures 2, 4, 5, 7, and 8.

x_i	y_i	a	b	R	Figure
$(E_{def}\,(TiO_2)_5$	E_{ads}	–7.61	–0.42	0.78	Fig. 2
ΔQ	E_{ads}	–6.28	1.50	0.88	Fig. 4
ΔQ	$E_{def}\,(TiO_2)_5$	–0.60	–2.88	0.91	Fig. 5
Φ M_2C	E_{ads}	–46.51	7.25	0.86	Fig. 7 (a)
Φ M_2C	$E_{def}\,(TiO_2)_5$	70.82	–12.93	0.80	Fig. 7 (b)
ΔQ	Φ M_2C	5.17	0.16	0.83	Fig. 7 (c)
χ_M	E_{ads}	–24.85	6.59	0.89	Fig. 8 (a)
χ_M	$E_{def}\,(TiO_2)_5$	32.01	–11.65	0.83	Fig. 8 (b)
ε_d	E_{ads}	–11.70	–1.22	0.87	Fig. 8 (c)
ε_d	$E_{def}\,(TiO_2)_5$	8.57	2.28	0.85	Fig. 8 (d)

Fig. S1. Atomic models of isolated and anchored $(TiO_2)_5$ clusters. Bond lengths (pink color) and bond angles (blue color) in the isolated $(TiO_2)_5$ cluster (top panel) compared to the deformed titania cluster in the $(TiO_2)_5/M_2C$ composite structures (bottom panels), corresponding to the most stable configuration for each $(TiO_2)_5/M_2C$. The color scheme of the $(TiO_2)_5$ cluster is the same as described in Fig. 1.



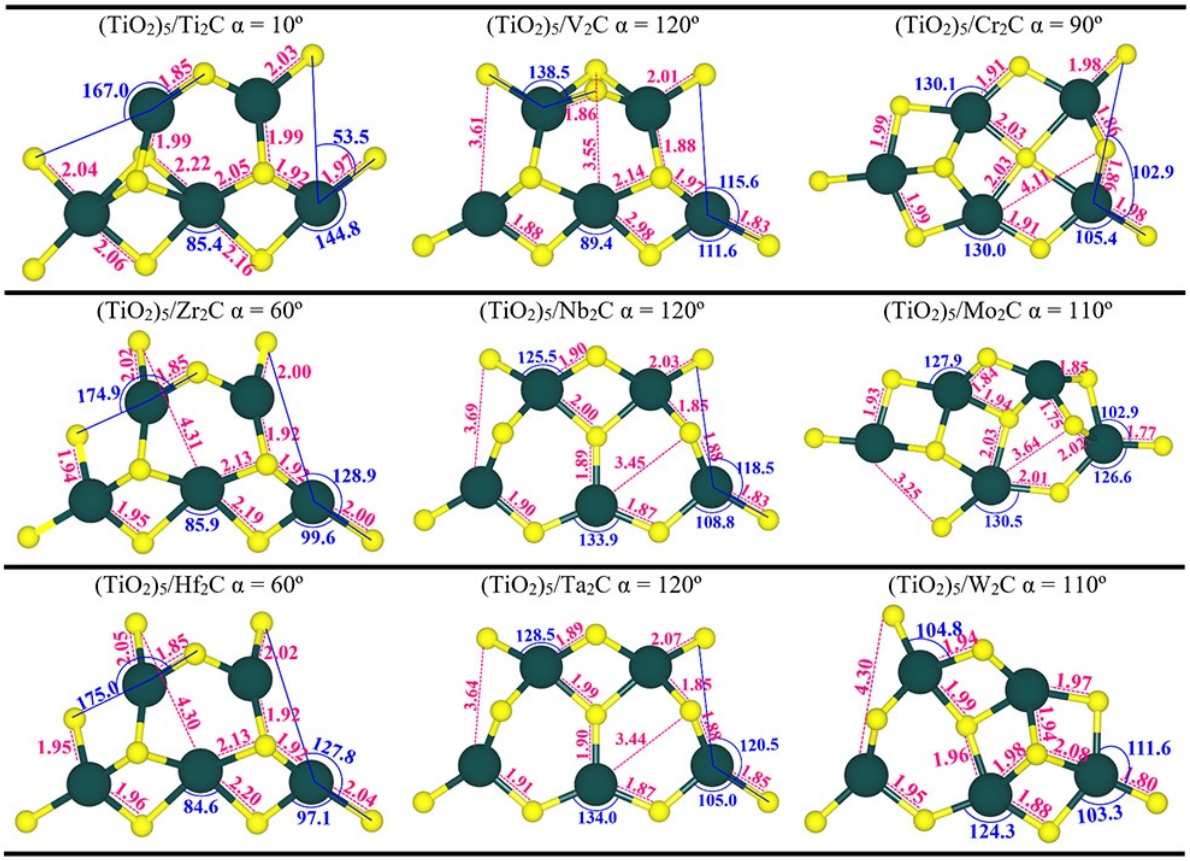


Fig. S2. Projected DOS per atomic orbital (in states/eV) for (a) $p(5\times5)$ $(TiO_2)_5/Ti_2C$, (b) $p(5\times5)$ $(TiO_2)_5/Zr_2C$, (c) $p(5\times5)$ $(TiO_2)_5/Hf_2C$, (d) $p(5\times5)$ $(TiO_2)_5/V_2C$, (e) $p(5\times5)$ $(TiO_2)_5/Nb_2C$, (f) $p(5\times5)$ $(TiO_2)_5/Ta_2C$, (g) $p(5\times5)$ $(TiO_2)_5/Cr_2C$, (h) $p(5\times5)$ $(TiO_2)_5/Mo_2C$, and (i) $p(5\times5)$ $(TiO_2)_5/W_2C$. The energies are referenced to the vacuum level (E_V) (dashed black line in eV).