Supplementary information

Insight into point defects in β-Mo2C and carbide evolution from first principles

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Figures

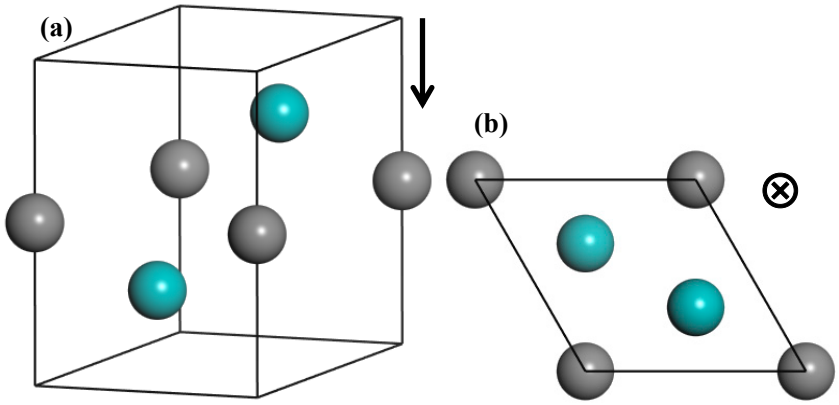


Figure S1 Schematic diagram of Mo2C structure of unit cell (a) and along (b) [0001] direction.

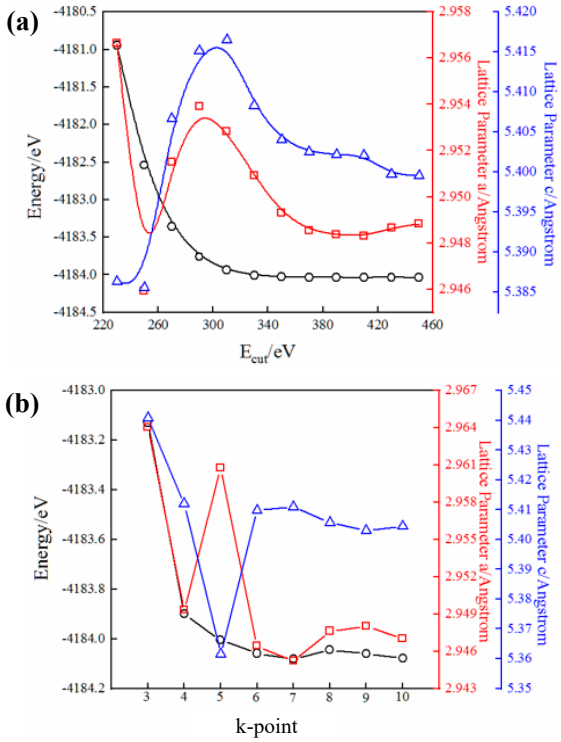


Figure S2 Convergence tests for Mo2C unit cell: Change of total energy and lattice parameter for Mo2C with different (a) cutoff energies and (b) k-points.

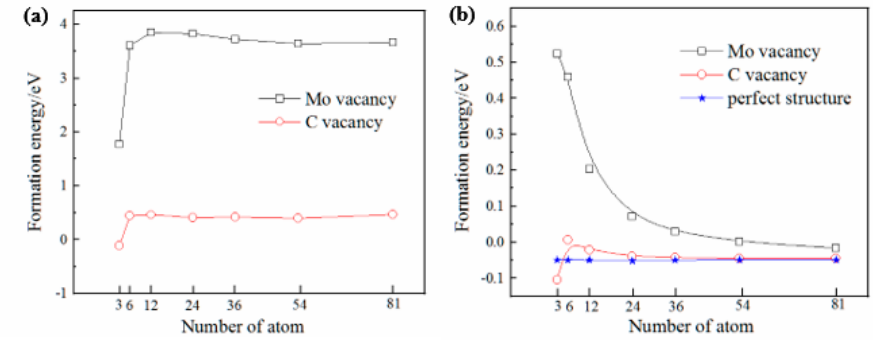
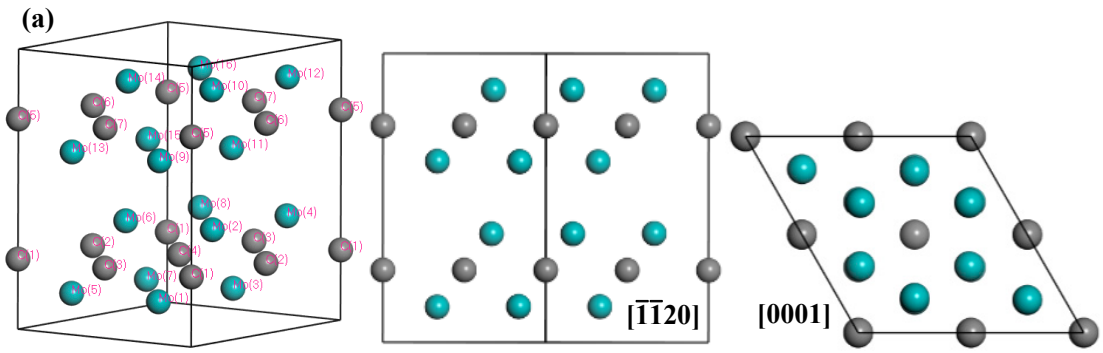


Figure S3 Convergence test for Mo2C supercell: (a) formation energy of vacancy, (b) formation energy of bulk material with vacancy.



(b)

Mulliken atomic populations for V_C

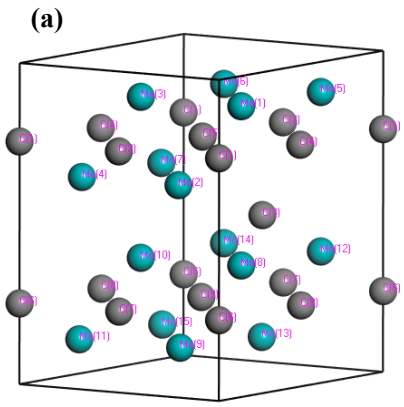
Species	No.	s	p	d	f	Total	Charge(e)
C	1	1.44	3.17	0	0	4.6	-0.6
C	2	1.44	3.17	0	0	4.61	-0.61
C	3	1.44	3.17	0	0	4.61	-0.61
C	4	1.43	3.18	0	0	4.61	-0.61
C	5	1.44	3.18	0	0	4.62	-0.62
C	6	1.44	3.18	0	0	4.62	-0.62
C	7	1.44	3.18	0	0	4.62	-0.62
Mo	1	2.21	6.63	4.88	0	13.72	0.28
Mo	2	2.21	6.63	4.88	0	13.72	0.28
Mo	3	2.21	6.63	4.88	0	13.72	0.28
Mo	4	2.21	6.64	4.87	0	13.72	0.28
Mo	5	2.21	6.64	4.87	0	13.72	0.28
Mo	6	2.21	6.63	4.88	0	13.72	0.28
Mo	7	2.21	6.63	4.88	0	13.72	0.28
Mo	8	2.21	6.63	4.88	0	13.72	0.28
Mo	9	2.22	6.63	4.89	0	13.74	0.26
Mo	10	2.22	6.63	4.89	0	13.74	0.26
Mo	11	2.22	6.63	4.89	0	13.74	0.26
Mo	12	2.21	6.66	4.87	0	13.74	0.26
Mo	13	2.21	6.66	4.87	0	13.74	0.26
Mo	14	2.22	6.63	4.89	0	13.74	0.26
Mo	15	2.22	6.63	4.89	0	13.74	0.26
Mo	16	2.22	6.63	4.89	0	13.74	0.26

(c)

Bond populations for V_C

Bond	Population	Length(Å)	Bond	Population	Length(Å)
C 7 Mo 12	0.41	2.08871	C 3 Mo 1	0.33	2.10658
C 6 Mo 12	0.41	2.08871	C 3 Mo 4	0.34	2.11224
C 7 Mo 13	0.41	2.08871	C 2 Mo 4	0.34	2.11224
C 6 Mo 13	0.41	2.08871	C 3 Mo 5	0.34	2.11224
C 5 Mo 12	0.41	2.09045	C 2 Mo 5	0.34	2.11224
C 5 Mo 13	0.41	2.09046	C 1 Mo 4	0.33	2.11324
C 4 Mo 2	0.32	2.10123	C 1 Mo 5	0.33	2.11325
C 4 Mo 8	0.32	2.10123	C 5 Mo 16	0.28	2.12091
C 4 Mo 7	0.32	2.10123	C 5 Mo 10	0.28	2.12091
C 4 Mo 1	0.32	2.10123	C 5 Mo 9	0.28	2.12091
C 4 Mo 6	0.32	2.10288	C 5 Mo 15	0.28	2.12091
C 4 Mo 3	0.32	2.10289	C 6 Mo 14	0.28	2.12125
C 1 Mo 8	0.33	2.10557	C 7 Mo 14	0.28	2.12125
C 1 Mo 2	0.33	2.10557	C 6 Mo 11	0.28	2.12125
C 1 Mo 1	0.33	2.10557	C 7 Mo 11	0.28	2.12125
C 1 Mo 7	0.33	2.10557	C 7 Mo 16	0.28	2.12161
C 2 Mo 6	0.33	2.10578	C 6 Mo 10	0.28	2.12161
C 2 Mo 6	0.33	2.10578	C 7 Mo 9	0.28	2.12161
C 1 Mo 3	0.33	2.10578	C 6 Mo 15	0.28	2.12161
C 3 Mo 3	0.33	2.10578			
C 3 Mo 8	0.33	2.10657			
C 2 Mo 2	0.33	2.10657			
C 2 Mo 7	0.33	2.10658			

Figure S4 Structure model of Mo2C supercell with V_C after optimization (a), as well as atomic population (b) and bond population (c).



(b)

Mulliken atomic populations for S_C

Species	No.	s	p	d	f	Total	Charge(e)
C	1	1.45	3.18	0	0	4.63	-0.63
C	2	1.46	3.08	0	0	4.54	-0.54
C	3	1.55	2.83	0	0	4.37	-0.37
C	4	1.46	3.08	0	0	4.54	-0.54
C	5	1.46	3.08	0	0	4.54	-0.54
C	6	1.44	3.18	0	0	4.62	-0.62
C	7	1.43	3.17	0	0	4.6	-0.6
C	8	1.43	3.17	0	0	4.6	-0.6
C	9	1.44	3.17	0	0	4.6	-0.6
Mo	1	2.25	6.55	4.85	0	13.65	0.35
Mo	2	2.28	6.53	4.86	0	13.67	0.33
Mo	3	2.18	6.48	4.91	0	13.57	0.43
Mo	4	2.28	6.53	4.86	0	13.67	0.33
Mo	5	2.25	6.55	4.85	0	13.65	0.35
Mo	6	2.25	6.55	4.85	0	13.65	0.35
Mo	7	2.28	6.53	4.86	0	13.67	0.33
Mo	8	2.24	6.54	4.88	0	13.66	0.34
Mo	9	2.2	6.58	4.88	0	13.66	0.34
Mo	10	2.25	6.68	4.91	0	13.84	0.16
Mo	11	2.2	6.58	4.88	0	13.65	0.35
Mo	12	2.24	6.54	4.89	0	13.66	0.34
Mo	13	2.22	6.55	4.89	0	13.66	0.34
Mo	14	2.24	6.54	4.88	0	13.66	0.34
Mo	15	2.2	6.58	4.88	0	13.66	0.34

(c)

Bond populations for S_C

Bond	Population	Length(Å)	Bond	Population	Length(Å)
C 3 Mo 12	0.64	2.03441	C 8 Mo 12	0.34	2.11443
C 3 Mo 8	0.63	2.04036	C 7 Mo 12	0.34	2.11451
C 3 Mo 14	0.63	2.04045	C 9 Mo 14	0.34	2.11453
C 2 Mo 2	0.53	2.04477	C 7 Mo 14	0.34	2.11458
C 4 Mo 7	0.53	2.04477	C 8 Mo 8	0.34	2.11459
C 4 Mo 4	0.53	2.04605	C 9 Mo 8	0.34	2.11462
C 2 Mo 4	0.53	2.04613	C 1 Mo 7	0.32	2.11832
C 5 Mo 2	0.53	2.04635	C 1 Mo 2	0.32	2.1184
C 5 Mo 7	0.53	2.04643	C 1 Mo 4	0.31	2.11871
C 6 Mo 11	0.36	2.05717	C 9 Mo 10	0.28	2.13068
C 6 Mo 15	0.36	2.06009	C 7 Mo 10	0.28	2.13075
C 6 Mo 9	0.36	2.06017	C 8 Mo 10	0.28	2.13083
C 2 Mo 6	0.42	2.07967	C 1 Mo 1	0.33	2.14064
C 4 Mo 1	0.42	2.07967	C 1 Mo 6	0.33	2.14073
C 4 Mo 5	0.42	2.08149	C 1 Mo 5	0.33	2.14083
C 2 Mo 5	0.42	2.08157	C 9 Mo 13	0.28	2.14121
C 5 Mo 6	0.42	2.08214	C 7 Mo 13	0.28	2.14133
C 5 Mo 1	0.42	2.08223	C 8 Mo 13	0.28	2.14142
C 8 Mo 15	0.37	2.08686	C 5 Mo 3	0.13	2.16837
C 7 Mo 9	0.37	2.08686	C 2 Mo 3	0.13	2.16991
C 8 Mo 11	0.37	2.08729	C 4 Mo 3	0.13	2.17
C 7 Mo 11	0.37	2.08737	C 6 Mo 12	0.26	2.18092
C 9 Mo 9	0.37	2.0875	C 6 Mo 8	0.27	2.18278
C 9 Mo 15	0.37	2.08758	C 6 Mo 14	0.27	2.18288

Figure S5 3D structure model of Mo2C supercell with S_C after optimization (a), as well as atomic population (b) and bond population (c).

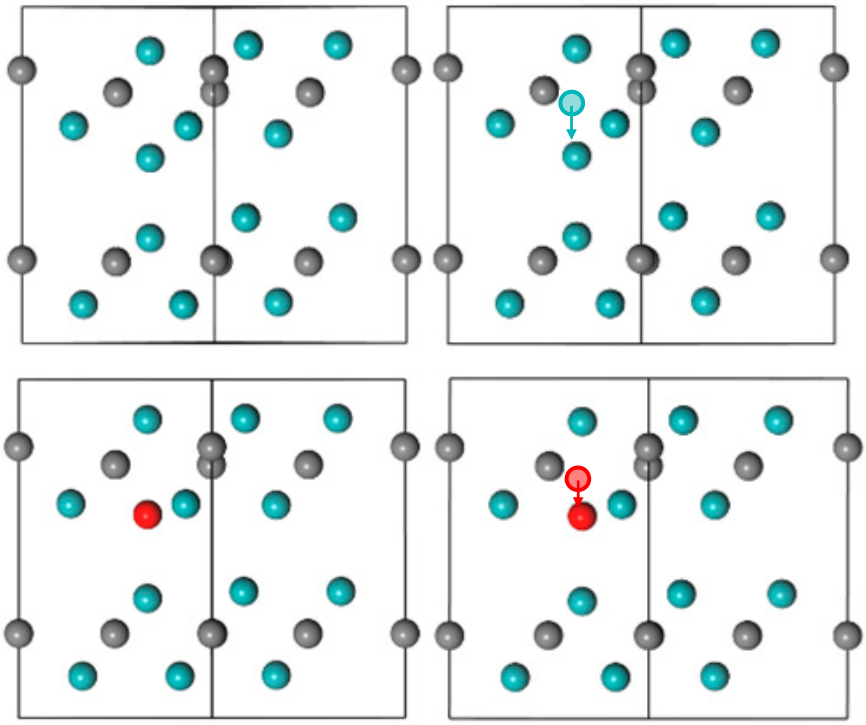


Figure S6 Structure model of Mo2C supercell with interstitial atom after optimization: (a) I_{Mo}(I), (b) I_{Mo}(II), (c) I_V(I) and (d) I_V(II). Semitransparent cyan and red balls represent the original positon for Mo and V atom.

Tables

Table S1 Total energy for different Mo2C supercells with or without vacancy defects and energy for Mo and C atom (eV).

Supercell	$E_{perf}(N)$	$E^{def}_{vacancy}$		E(Mo)	E(C)
		V_{Mo}	V_C		
1×1×1	-4184.059	-2245.430	-4029.102	-1936.860	-155.071
1×1×2	-8368.118	-6427.65	-8212.604	-1936.860	-155.071
1×2×2	-16736.235	-14795.522	-16580.703	-1936.860	-155.071
2×2×2	-32232.884	-31531.833	-33317.045	-1936.860	-155.071
3×2×2	-50208.717	-48268.129	-50053.229	-1936.860	-155.071
3×3×2	-75313.075	-73372.568	-75157.606	-1936.860	-155.071
3×3×3	-112969.601	-111029.074	-112814.06	-1936.860	-155.071

Table S2 Calculated formation energy of vacancy and formation energy of bulk materials with vacancy (eV).

Supercell	$E^{def}_{vacancy}$		$E^{bulk}_{vacancy}$		
	V_{Mo}	V_C	V_{Mo}	V_C	perfect
1×1×1	5.132	0.930	0.239	-0.361	-0.433
1×1×2	5.050	0.402	-0.130	-0.440	-0.437
1×2×2	4.797	-0.088	-0.296	-0.453	-0.430
2×2×2	4.385	-0.880	-0.367	-0.451	-0.436
3×2×2	4.555	-0.726	-0.393	-0.449	-0.436
3×3×2	4.462	-0.803	-0.389	-0.45	-0.435
3×3×3	4.437	-0.907	-0.376	-0.448	-0.436

Table S3 Total energy for Mo2C supercells with substitution and interstitial defects (eV).

Defect type	$E_{perf}(N)$	E^{def}	
		Mo	C
Substation	-32232.884	-34007.186 (S_{Mo})	-30446.863 (S_C)
Interstitial	-32232.884	-34159.492 (I_{Mo}(I,II))	-32384.745 (I_C(I,II))

Table S4 Total energy for Mo2C supercells with V-related defects and energy for V atom (eV).

	$S_{V\text{-}Mo}$	$S_{V\text{-}C}$	I_V(I)	I_V(II)
E^{def}	-32273.271	-34048.676	34202.379	34201.550