Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Binding and activation of ethylene on tungsten carbide and platinum surfaces

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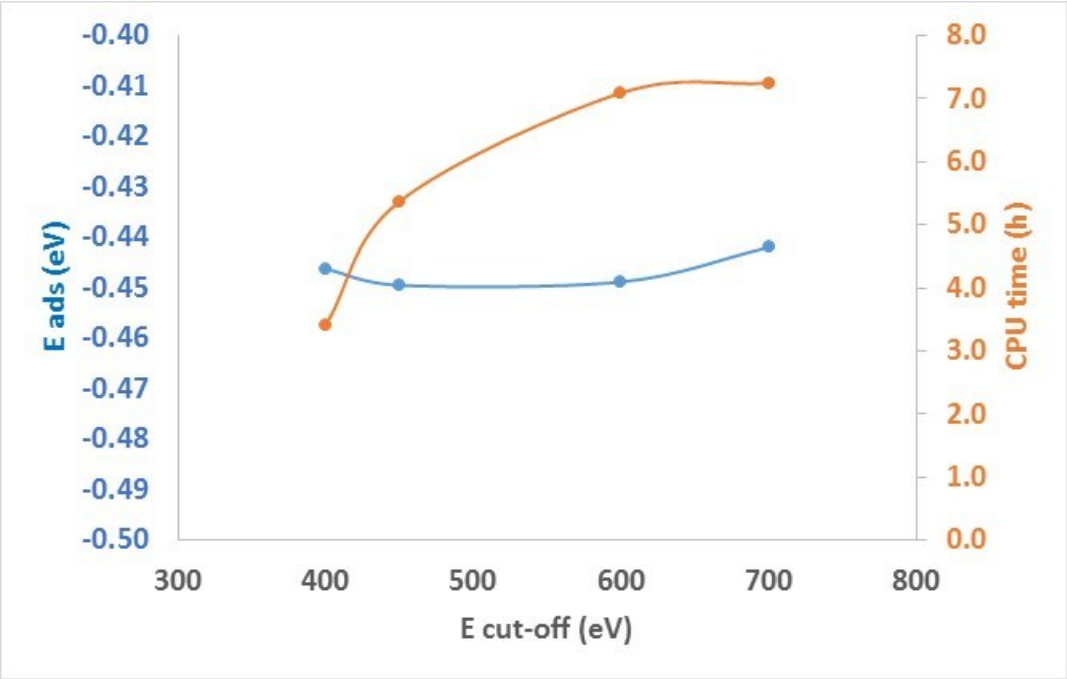
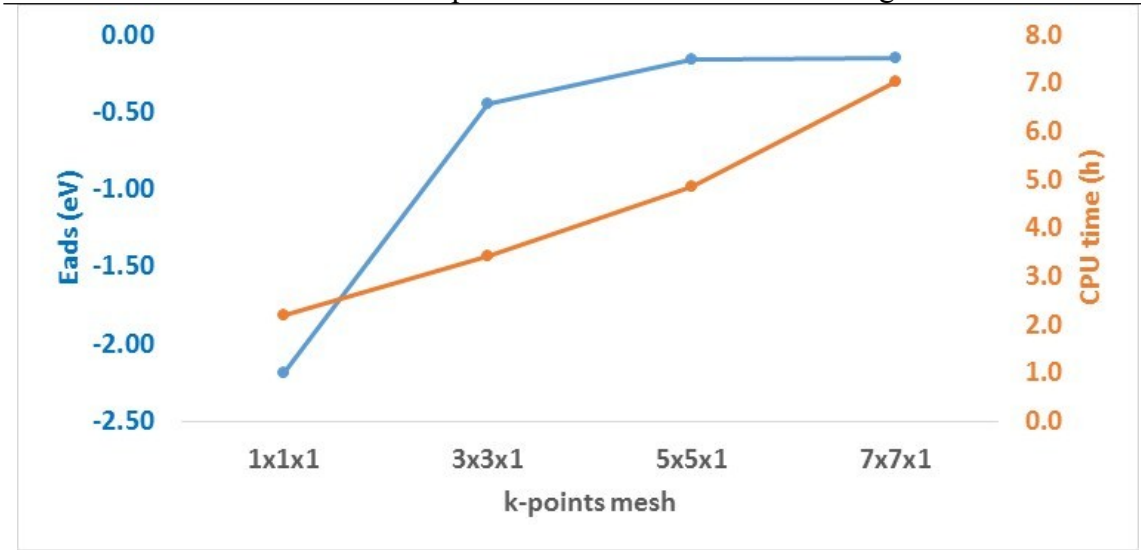


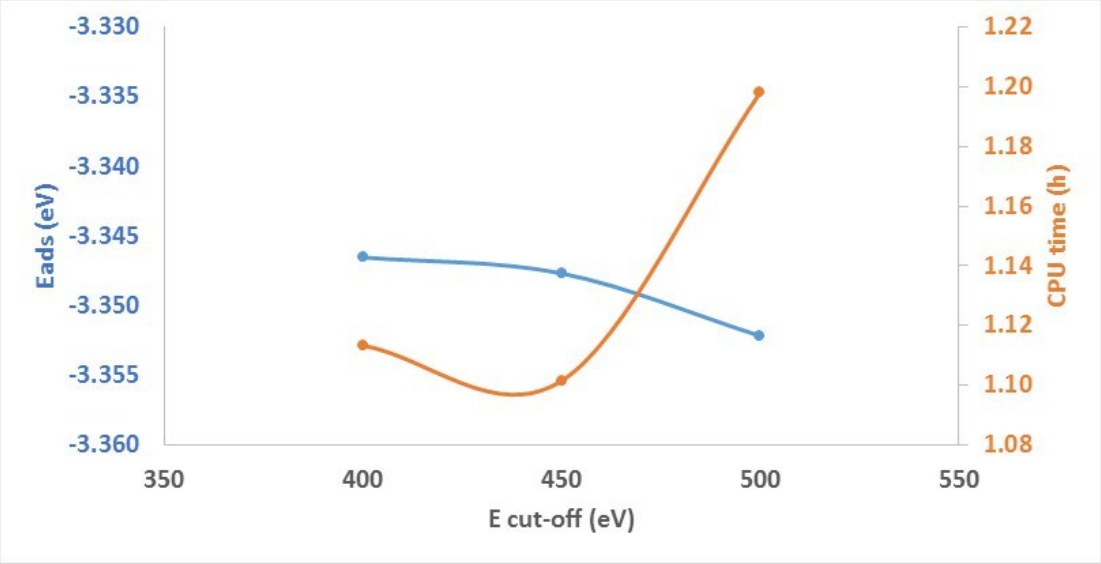
Constant **k**-points mesh = 3x3x1 for screening



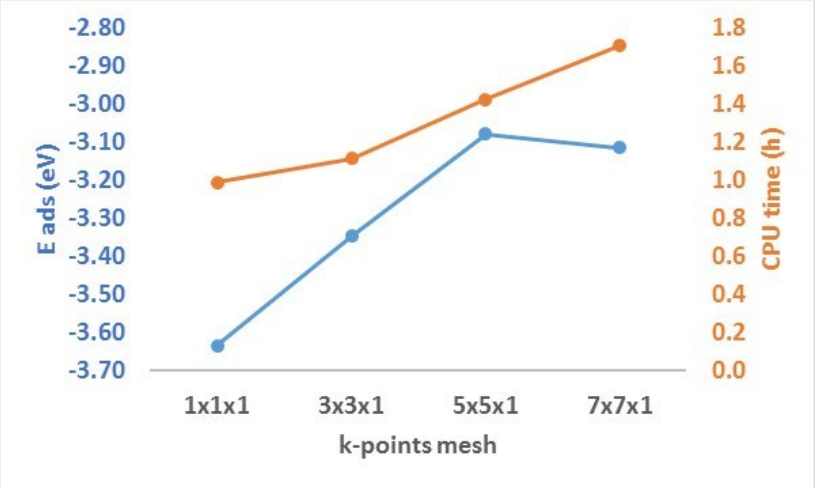
Constant cut-off energy = 400 eV for screening

*<u>Conclusions</u>: Cut-off energy = 400 eV, **k**-points mesh = 5x5x1*

Fig. S1. Establishment of the cut-off energy and **k**-points mesh for the adsorption of C_2H_4 on γ-WC(001) surface.



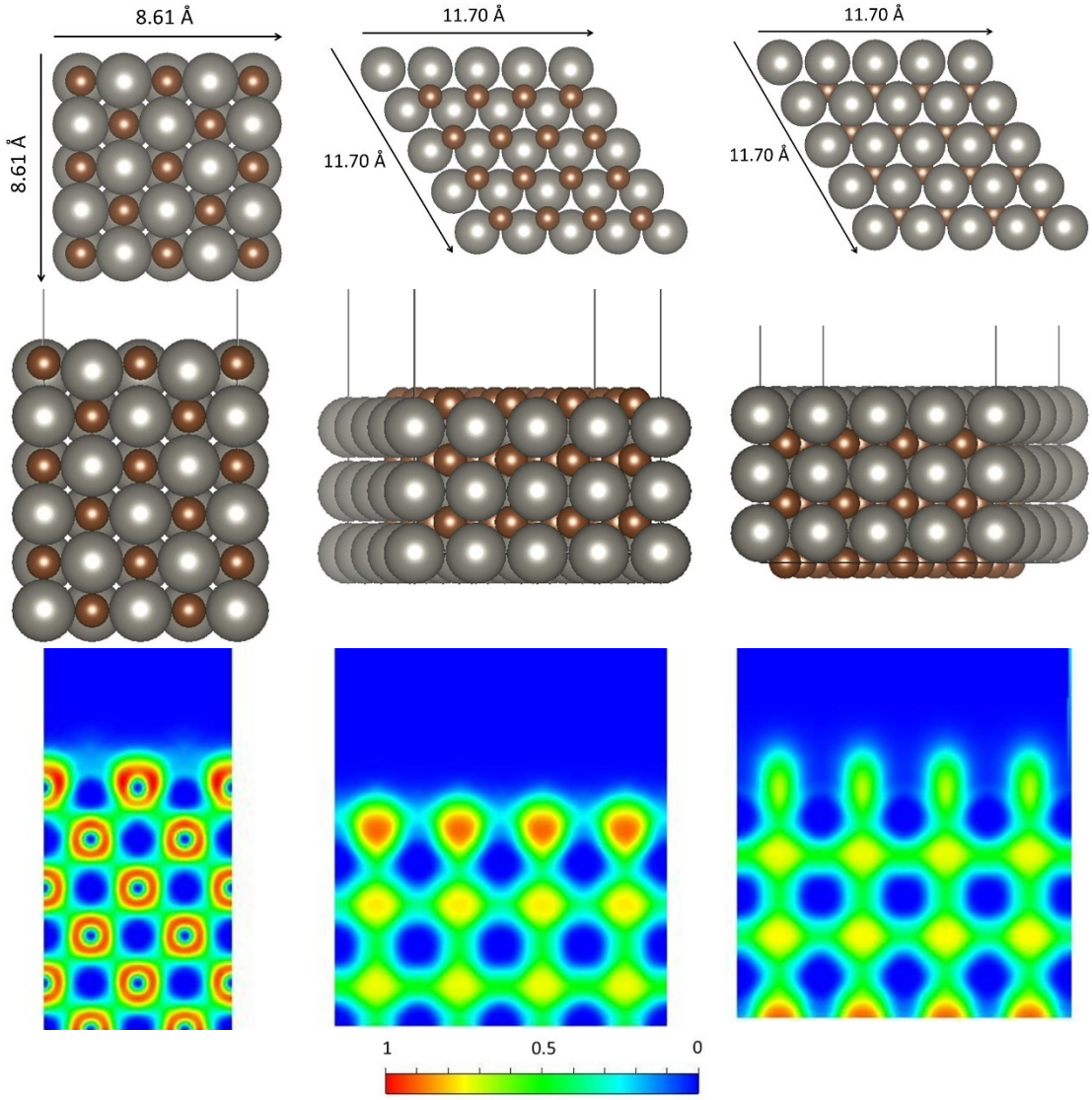
Constant **k**-points mesh = 3x3x1for screening



Constant cut-off energy = 400 eV for screening

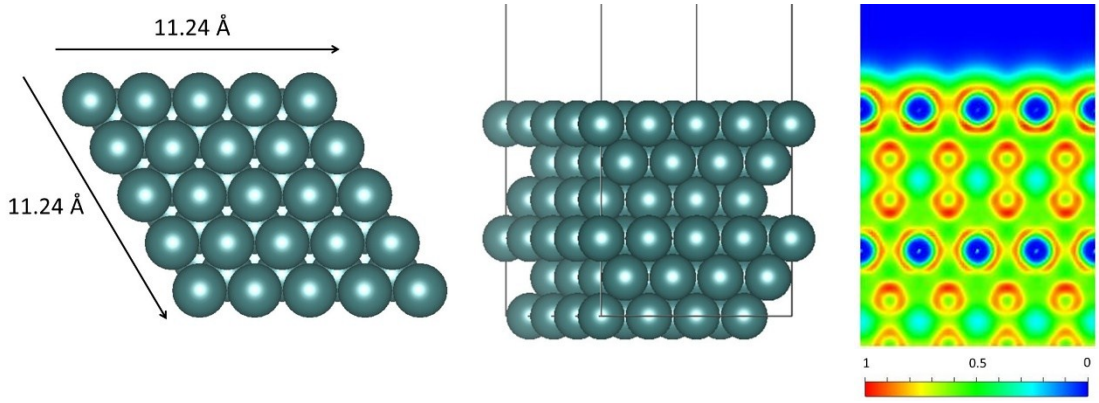
*<u>Conclusions</u>: Cut-off energy = 400 eV, **k**-points mesh = 5x5x1*

Fig. S2. Establishment of the cut-off energy and **k**-points mesh for the adsorption of C_2H_4 on α-WC(0001) surface.



a) γ-WC(001) b) α-WC-C c) γ-WC-W

Fig. S3. Geometry and electronic properties of the clean surfaces: a) γ-WC(001), b) α-WC-C, c) α-WC-W. Top: top view, middle: side view, bottom: ELF chart. Carbon and tungsten atoms are represented with brown and gray colors, respectively.



a) b) c)

Fig. S4. Geometry and electronic aspects of the clean Pt(111) surface. a) top view, b) side view, bottom: ELF.

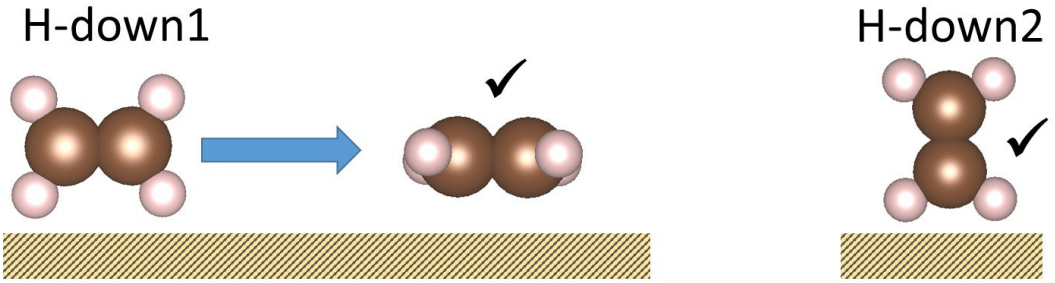


Fig. S5. Behavior of the binding on α-WC(0001) surface when H atoms are directed towards the surface.

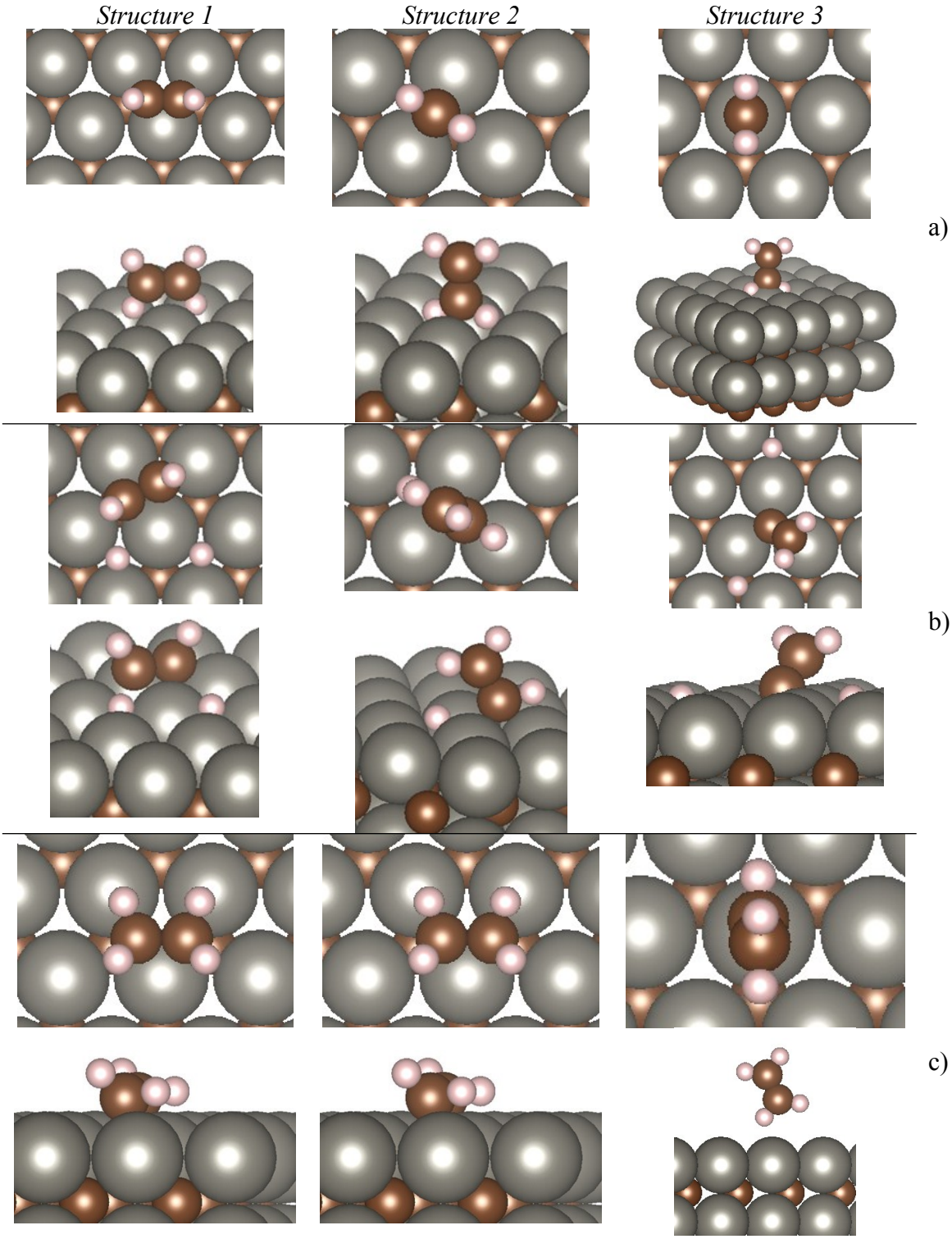


Fig. S6. Difference in adsorption geometries of three structures by using a 4-layers and 6-layers slabs for C_2H_4 binding on the α-WC-W surface. a) Input geometry; b) output, 4-layers; c) output, 6-layers. Top and side view is shown in every case.

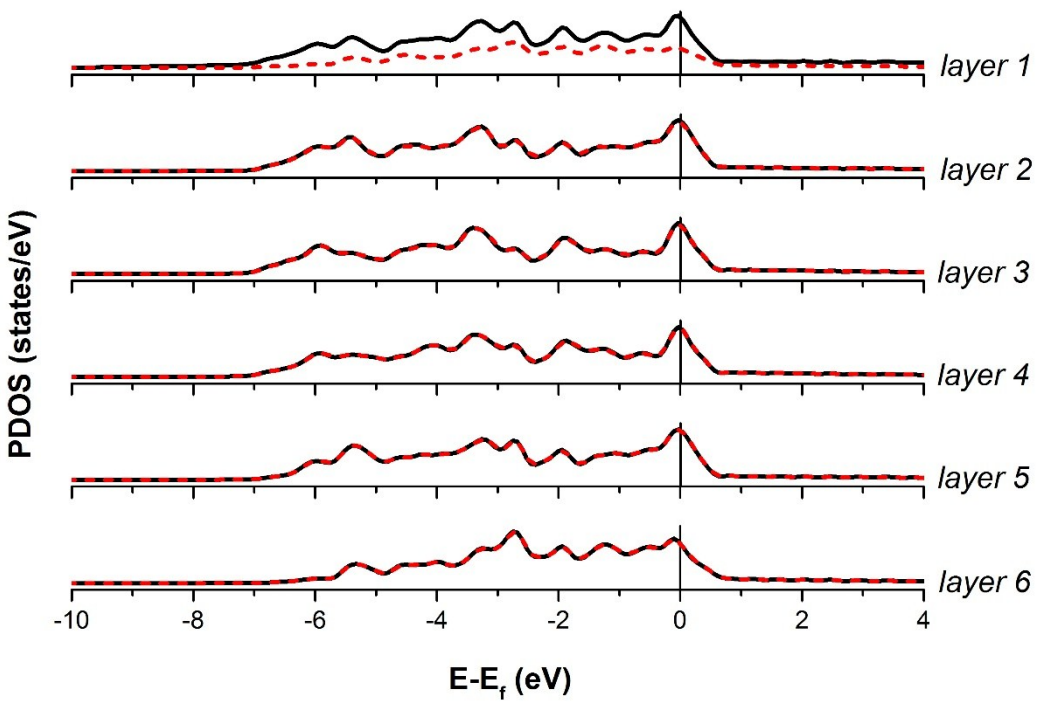


Fig. S7. *d*-band PDOS for every layer in Pt(111) surface slab. Black and red lines represent the PDOS before and after ethylene adsorption.

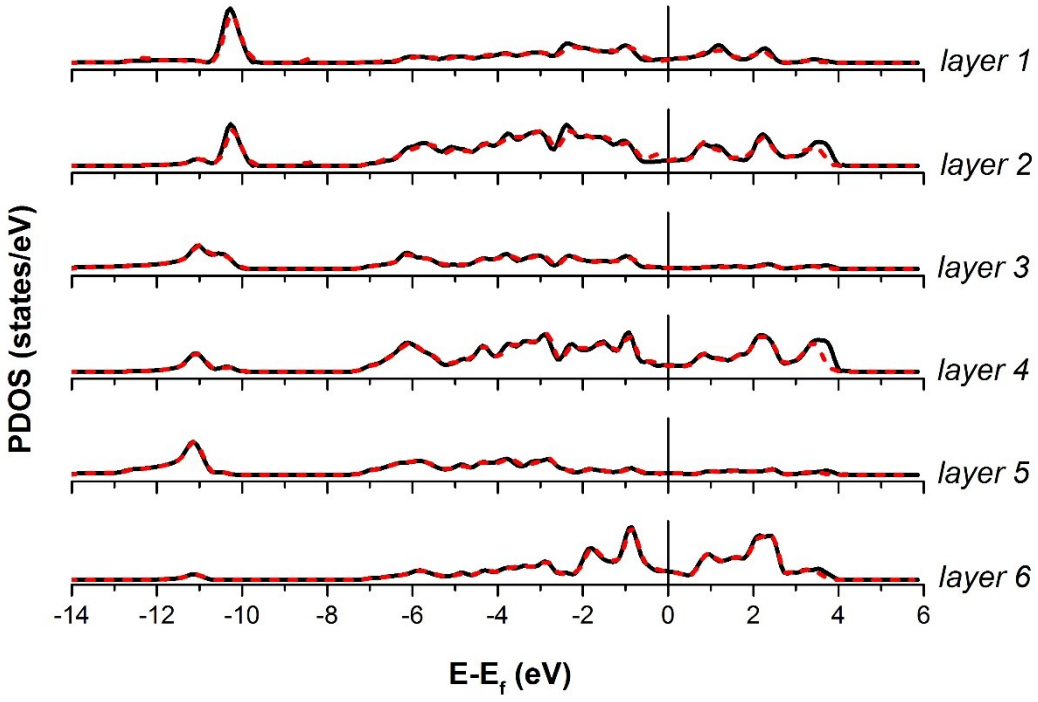


Fig. S8. PDOS for every layer in α-WC-C surface slab. The PDOS are *s,p*-bands for 1, 3, 5 layers, while *d*-band for 2, 4, 6 layers. Black and red lines represent the PDOS before and after ethylene adsorption.

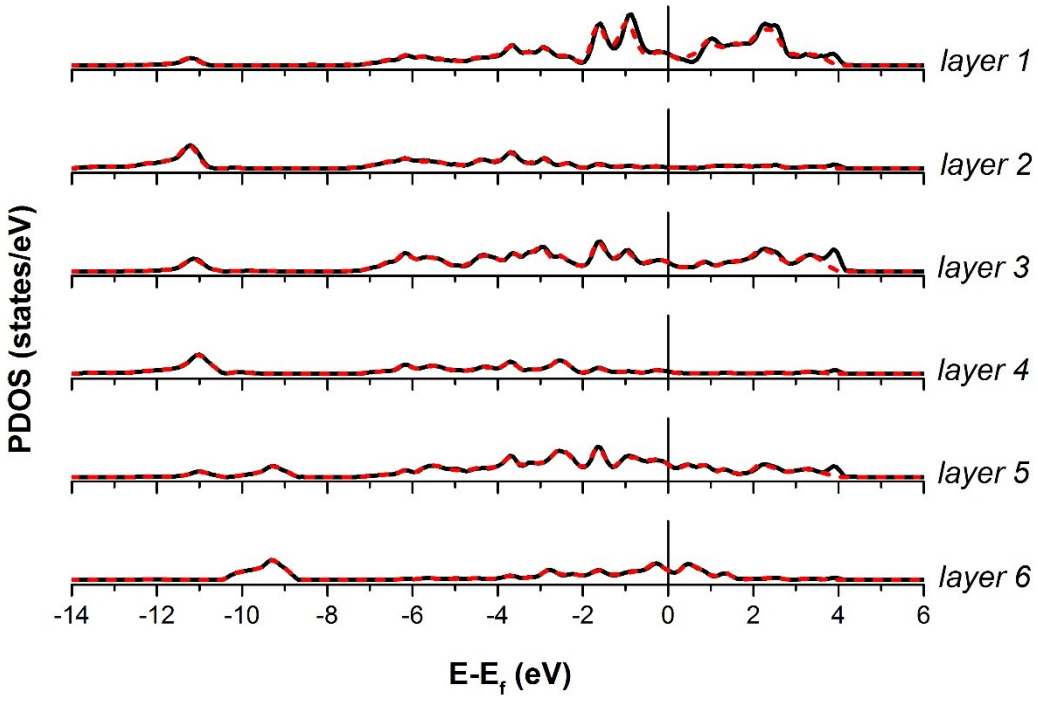


Fig. S9. PDOS for every layer in α-WC-W surface slab. The PDOS are *s,p*-bands for 1, 3, 5 layers, while *d*-band for 2, 4, 6 layers. Black and red lines represent the PDOS before and after ethylene adsorption.

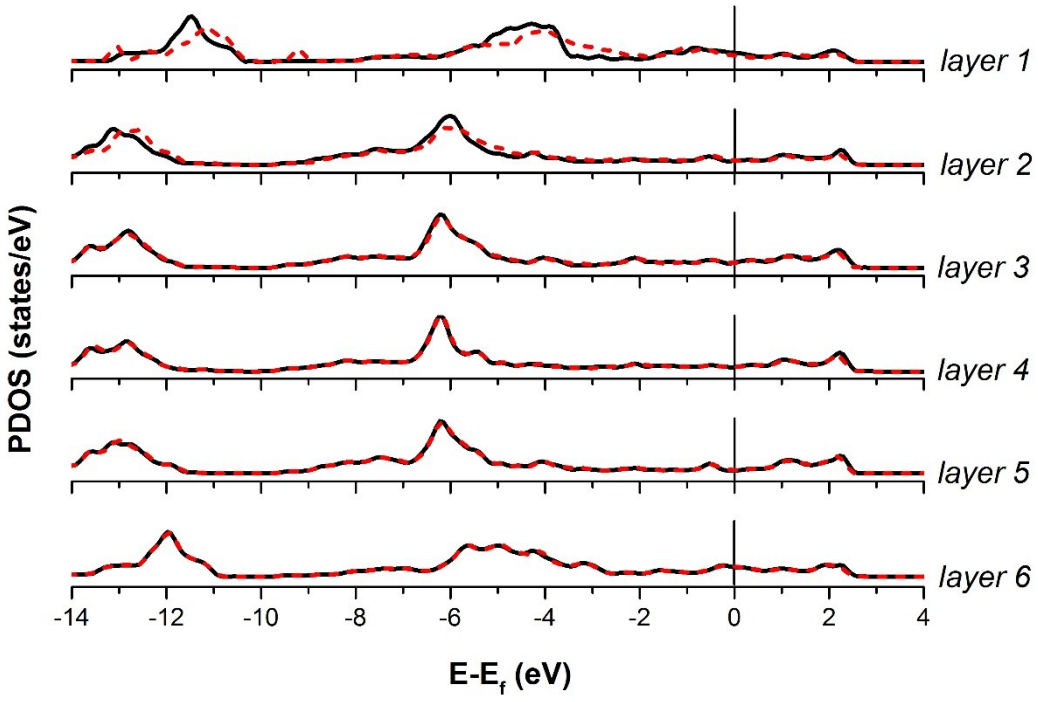


Fig. S10. *s,p*-PDOS for every layer in γ-WC(001) surface slab. Black and red lines represent the PDOS before and after ethylene adsorption.

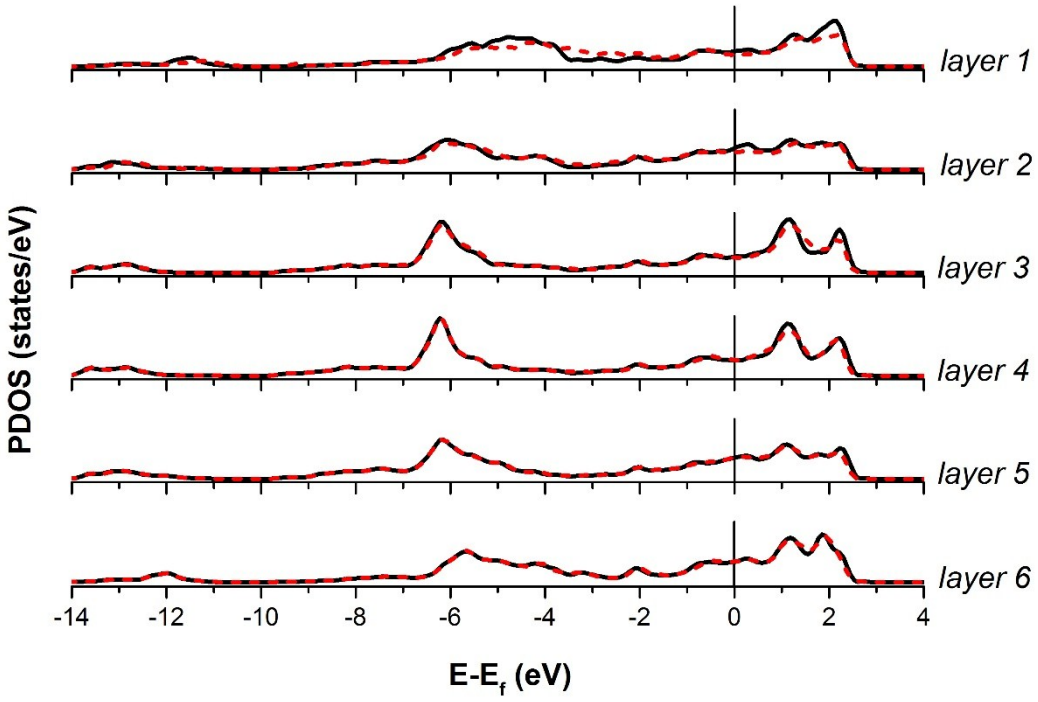


Fig. S11. *d*-PDOS for every layer in γ-WC(001) surface slab. Black and red lines represent the PDOS before and after ethylene adsorption.

Table S1. Energetics for ethylene adsorption and H_2 dissociative chemisorption on tungsten carbide surfaces, as a function of the number of layers in slab.

System	DFT and DFT +vdw energies (eV); vdW contributions	Number of layers in slab		
		4	6	8
C_2H_4 adsorption on α-WC-C	DFT	-3.12	-2.91	-2.91
	DFT+vdW	-3.55	-3.35	-3.35
	% vdW	12.1	13.3	13.3
C_2H_4 adsorption on α-WC-W	DFT	-1.88	-1.43	-1.42
	DFT+vdW	-2.42	-1.98	-1.98
	% vdW	22.5	27.8	-1.97
C_2H_4 adsorption on γ-WC(001)	DFT	-0.78	-0.37	-0.36
	DFT+vdW	-1.20	-0.87	-0.86
	% vdW	35.3	58.1	58.7
H_2 dissociative chemisorption reaction	DFT	-1.10	-1.02	-1.12
	DFT+vdW	-1.23	-1.18	-1.20
	% vdW	10.0	13.5	6.3

Table S2. Adsorption energies (Eq. 1) for ethylene binding on the γ-WC(001) surface.

Mode	DFT (eV)	DFT+vdW (eV)	% vdW	C-C[a] (Å)	C=C activation
di-σ-CC	**-0.72**	**-1.19**	**39.8**	**1.60**	✓
di-σ-CM	-0.37	-0.87	58.1	1.53	✓
π-M[b]	-0.25	-0.81	69.0	1.36	×
H-down1	-0.23	-0.62	62.0	1.33	×
H-down2	-0.23	-0.54	58.4	1.33	×
π-M[b]	-0.22	-0.78	71.2	1.35	×
H-down1	-0.22	-0.61	63.6	1.33	×
H-down2	-0.21	-0.55	61.1	1.33	×
di-σ-MM	-0.20	-0.70	72.1	1.52	✓
π-C[b]	0.03	-0.40	--	1.52	✓
π-C[b]	0.48	0.01	--	1.49	✓

[a] C=C bond length of free ethylene is 1.33 Å.

[b] Most stable structure in every case (π-M and π-C) has the $C_{ethylene}$-$C_{ethylene}$ bond axis parallel to $C_{surface}$-$C_{surface}$ bridge, while the other structure has it parallel to a W-W bridge.

Table S3. Ethylene adsorption energies (Eq. 1) on the α-WC(0001) surface

Mode	DFT (eV)	DFT+vdW (eV)	% vdW	C-C[a] (Å)	C=C activation
		α-WC-C			
di-σ-CC	**-2.91**	**-3.35**	**13.3**	**1.60**	✓
H-down2	-0.86	-1.35	36.4	1.33	×
π-C	0.02	-0.24	--	1.43	✓
		α-WC-W			
C-H, C-H	**-1.68**	**-2.24**	**24.9**	**1.50**	✓
C-H2	-1.43	-1.98	27.7	1.50	✓
H-down2	0.06	-0.25	--	1.33	×

[a] C=C bond length of free ethylene is 1.33 Å.

Table S4. Zero Point Energy (ZPE) term for absolute and adsorption energy for C_2H_4 binding on platinum and tungsten carbide surfaces. $E_{Non\text{-}ZPE}$ = Eq. 1, E_{ZPE} = Eq. 2

Surface	**Absolute energy**	**Adsorption energy**		
	% ZPE	**$E_{Non\text{-}ZPE}$ (eV)**	**E_{ZPE} (eV)**	**% ZPE**
Pt(111)	0.22	-1.78	-1.71	3.79
γ-WC(001)	0.15	-1.19	-0.87	36.77
α-WC-C	0.16	-3.35	-2.98	12.32
α-WC-W	0.13	-2.24	-2.25	0.53