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

Supplementary Information

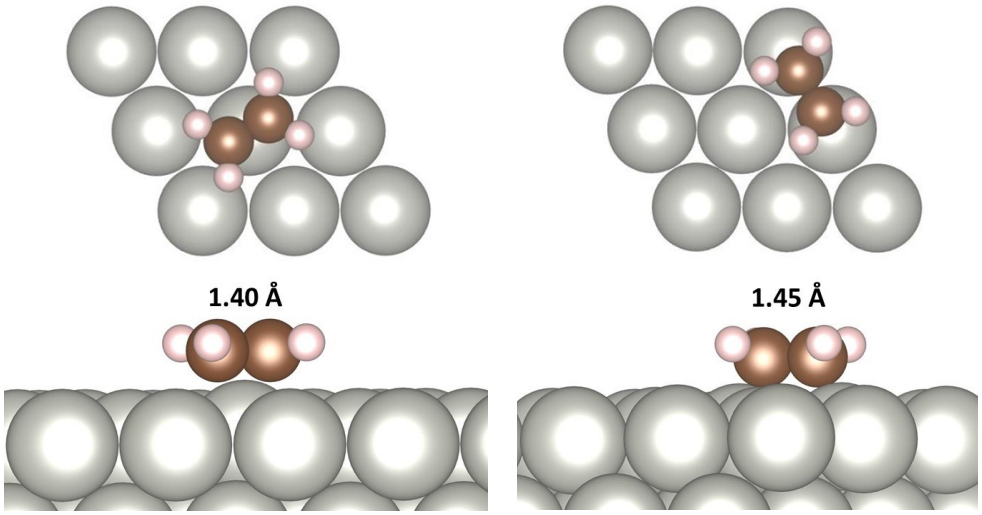
Acetylene adsorption on δ-MoC(001), TiC(001) and ZrC(001) surfaces: A comprehensive periodic DFT study

Carlos Jimenez-Orozco,[a] Elizabeth Florez,[b] Andres Moreno,[a] Ping Liu[c] and Jose A. Rodriguez*[c]

[a] Química de Recursos Energéticos y Medio Ambiente, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA; Calle 70 No. 52-21, Medellín, Colombia.

[b] Departamento de Ciencias Básicas, Universidad de Medellín, Carrera 87 No 30-65, Medellín, Colombia

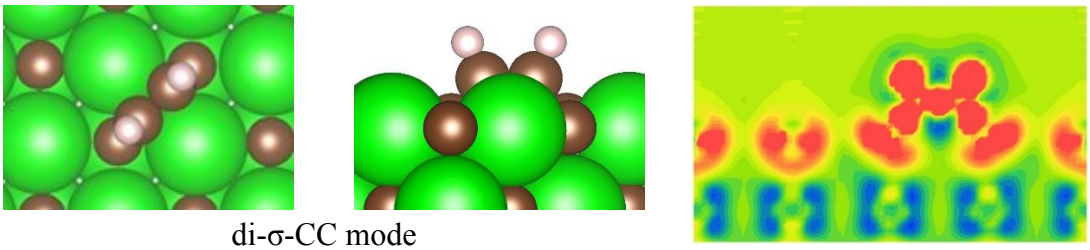
[c] Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA.



E_{ads}= -0.91 eV
a) π-M

E_{ads}= -1.10 eV
b) di-σ-MM

Figure S1. Ethylene adsorption modes on Pd(111) surface. Top: top view, bottom: side view. Numbers in each figure belongs to C-C bond length. C, brown; H, light beige; Pd, gray balls.



di-σ-CC mode

Top view Side view CDD plot

Figure S2. Most stable structure of C_2H_2 adsorbed on ZrC(001) surface. E_{ads}=-0.72 eV, Q_{ace}= -0.72e. C-C=1.47 Å.

Table S1. Adsorption modes involving one carbon (π-C) or metal (π-M) atom as starting structure.

E_{ads} (eV)	**Input[a]**	**Output[b]**	**C-C (Å)**
δ-MoC(001)			
-0.66	π-M, H-M	π-M, Hv-M	1.30
-0.70	π-M, H-C	π-M, Hv-C	1.30
-1.48	π-C, H-C	di-σ-MM, Hv	1.46
-0.79	π-C, H-M	di-σ-CM, Hv	1.40
TiC(001)			
-0.08	π-M, H-M	π-M, H-M	1.21
-0.10	π-M, H-C	π-M, H-C	1.22
-3.75	π-C, H-C	di-σ-CC, Hv	1.45
-0.76	π-C, H-M	μ-CM, Hv	1.39
ZrC(001)			
-0.13	π-M, H-M	π-M, H-M	1.22
-0.17	π-M, H-C	π-M, H-C	1.22
-1.64	π-C, H-C	σ-C, Hv	1.39
0.05	π-C, H-M	π-C, Hv-M	1.32

[a] H-C, H-M indicates that both acetylene H atoms are poiting toward $C_{surface}$ or metal atoms, respectively, from a top view.

[b] Hv indicates that H atoms are pointing towards the vacuum.

Table S2. Acetylene adsorption energies on TMC(001) surfaces. Results obtained without (DFT) and with vdW (DFT+vdW) correction to the electronic energy.[a]

δ-MoC(001)			TiC(001)			ZrC(001)		
DFT (eV)	DFT+vdW (eV)	Geometry[b]	DFT (eV)	DFT+vdW (eV)	Geometry[b]	DFT (eV)	DFT+vdW (eV)	Geometry[b]
-1.78	-2.35	di-σ-CM	-3.75	-4.16	di-σ-CC	-3.69	-4.08	di-σ-CC
-1.48	-2.15	di-σ-MMC[c]	-0.76	-1.16	μ-CM	-1.64	-2.06	σ-C
-0.83	-1.60	π-M	-0.10	-0.39	π-M	-0.19	-0.64	σ-C
-0.79	-1.33	di-σ-CM [d]	-0.08	-0.38	π-M	-0.17	-0.47	π-M
-0.70	-1.47	π-M	-0.02	-0.18	Top-C	-0.13	-0.42	π-M
-0.66	-1.41	π-M	0.04	-0.17	di-σ-MM	-0.01	-0.34	μ-CM
-0.53	-0.95	Top-h	0.05	-0.08	Top-M	0.00	-0.20	Top-h
-0.46	-0.88	Top-M	0.07	-0.12	Top-h	0.03	-0.18	Top-C
-0.42	-0.98	di-σ-MM				0.05	-0.40	π-C
-0.15	-0.39	Top-C				0.11	-0.16	di-σ-MM
-0.07	-0.57	di-σ-CC				0.12	-0.02	Top-M

[a] vdW corrections were carried out using the dispersion correction developed by Grimme (S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799) as implemented in CASTEP 5.5.

[b] see Table S1.

[c] Threefold interaction with one $C_{surface}$ and two Mo atoms.

[d] Hydrogen atoms non-eclipsed under a Newman projection.