Adsorpcija

Sadržaj 1.3.

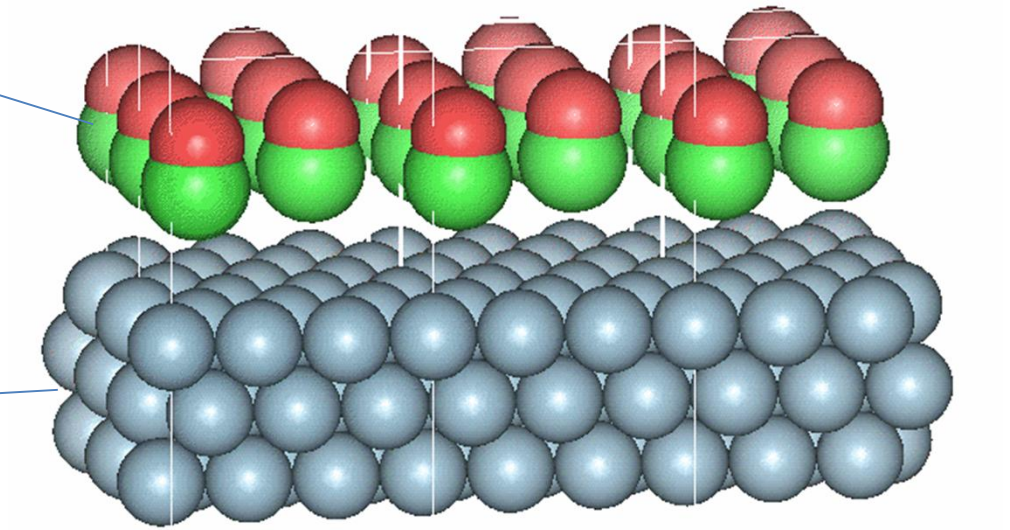
– Šta je pokreće
– Kako izgledaju adsorbovani slojevi
– Adsorpcioni trendovi

Key Terms

Adsorbat

Adsorbens

Substrat



http://chsfpc5.chem.ncsu.edu/~franzen/CH795N/dft_modules/surface_module/ni_111_co_binding.htm

Overview

Fizičke sile - fizisorpcija

Dipol-dipol

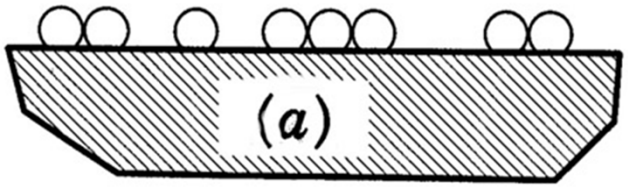
korelacija

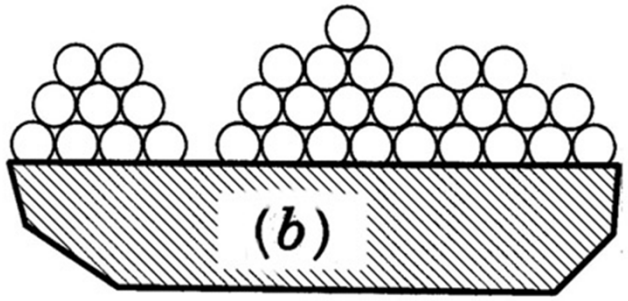
Hemijske sile – hemisorpcija

preraspodela naelektrisanja

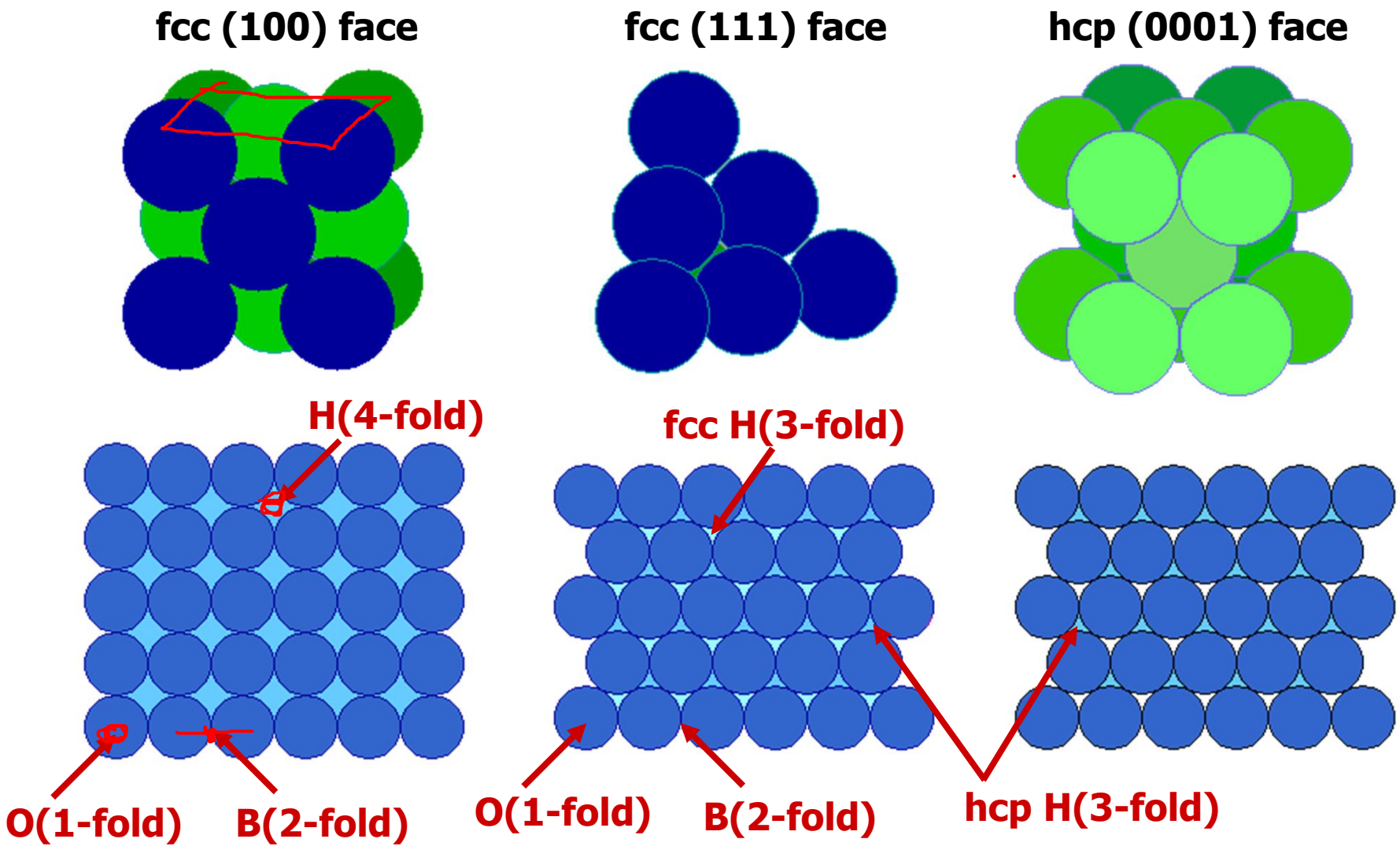
Gustine slične tečnostima

(1 gm/cm^3)=10^{15} molekula/cm^2



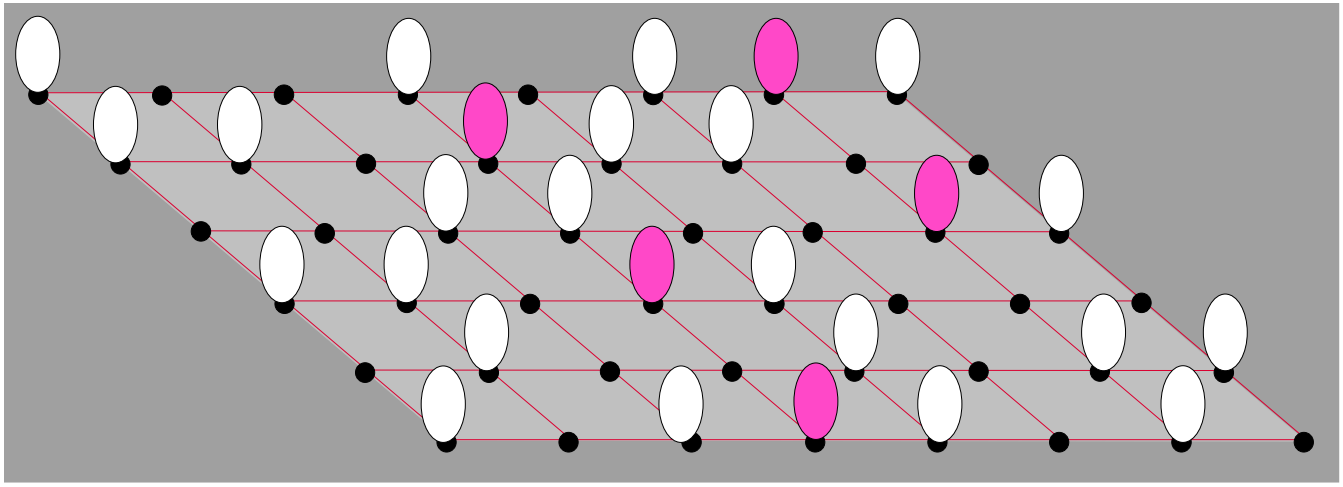


Adsorpciona mesta



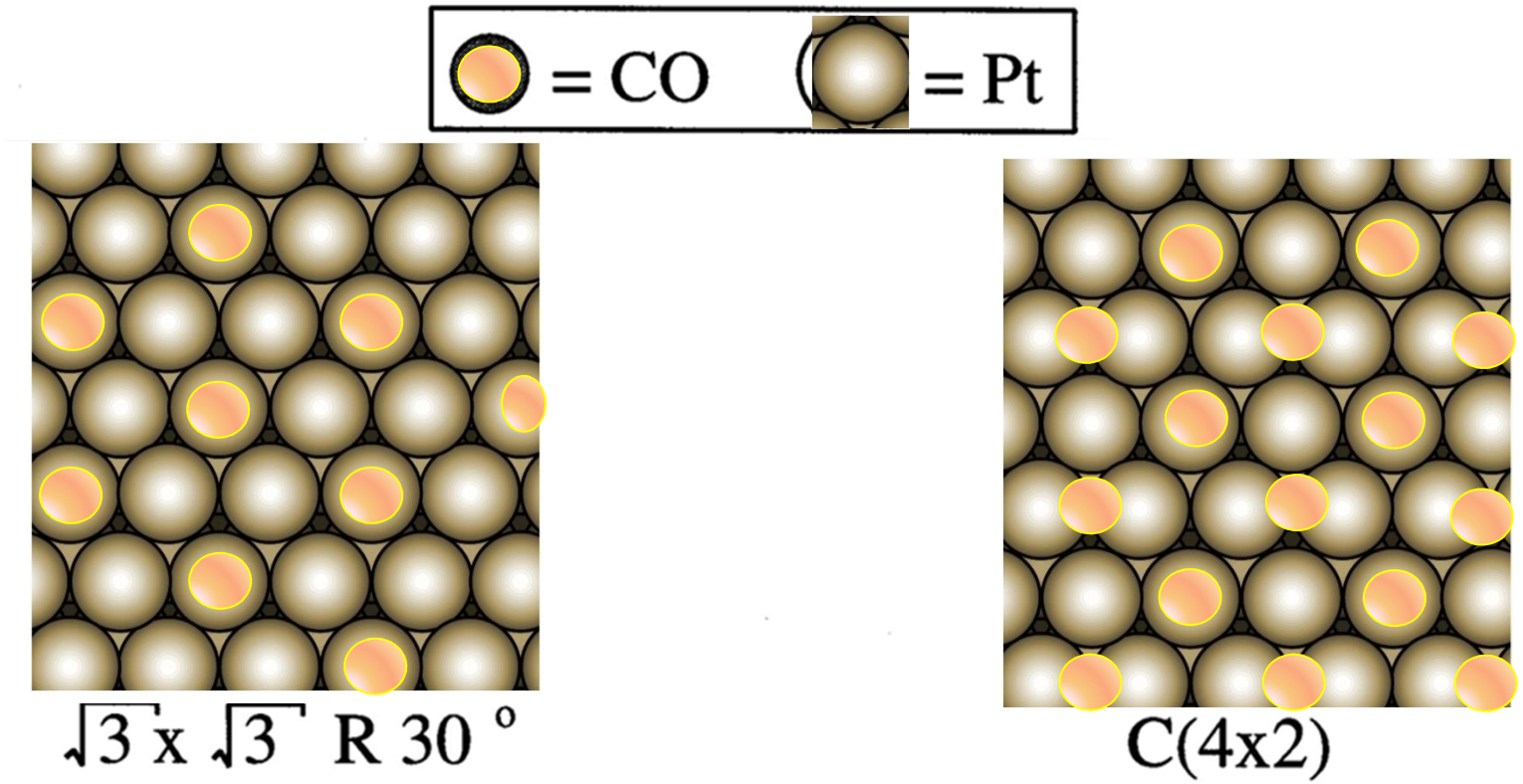
Geometrija adsorbovanih slojeva

Struktura adsorbovanih slojeva je uslovljena strukturom substrata



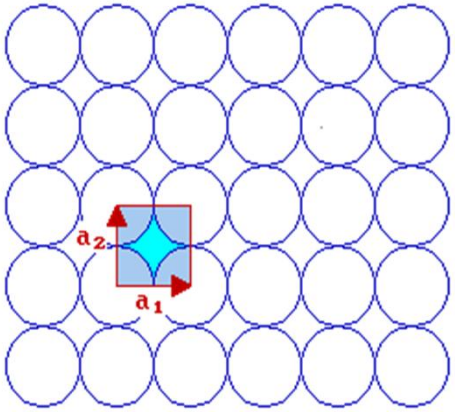
Lengmirovov tip adsorpcije na čvrstoj površini

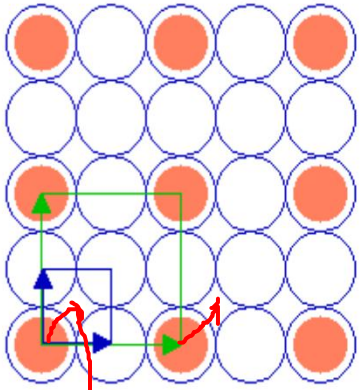
CO na Pt(111)



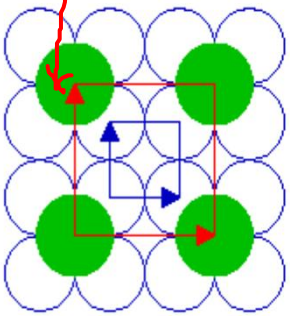
Crossley & King [1980]

fcc (100) face

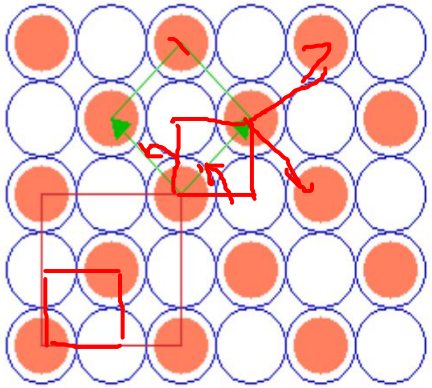




Substrate : fcc(100)
Substrate unit cell
Adsorbate unit cell

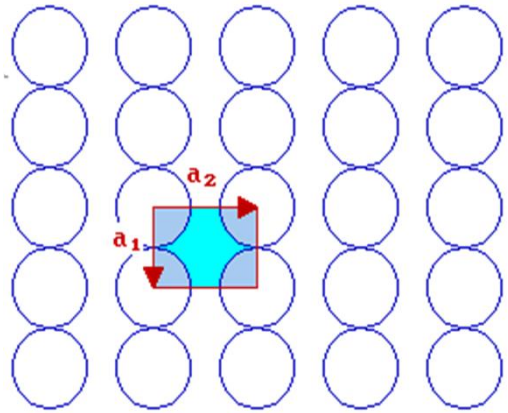


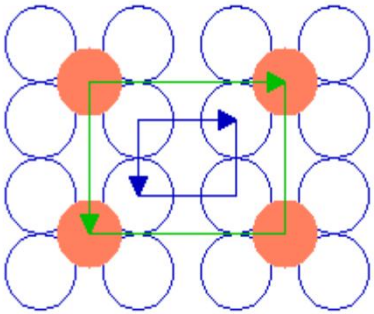
Substrate : fcc(100)
Substrate unit cell
Adsorbate unit cell



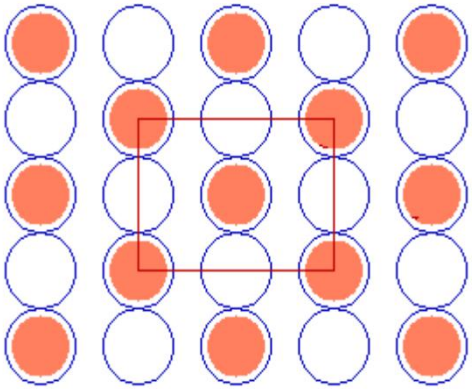
Substrate : fcc(100)
c(2 x 2)
(√2 x √2)R45

fcc (110) face



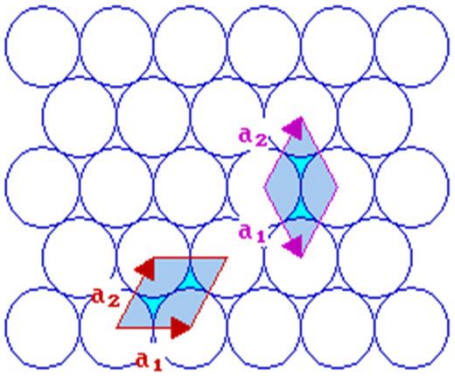


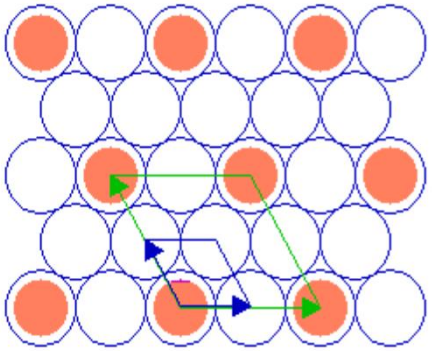
Substrate : fcc(110)
Substrate unit cell
Adsorbate unit cell



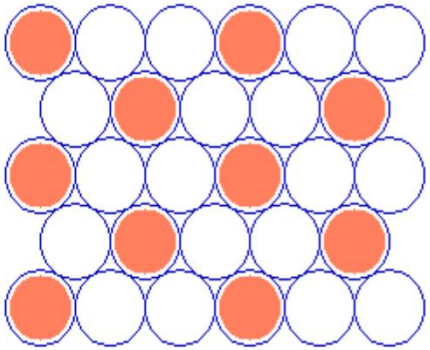
Substrate : fcc(110)
c(2 x 2)

fcc (111) face



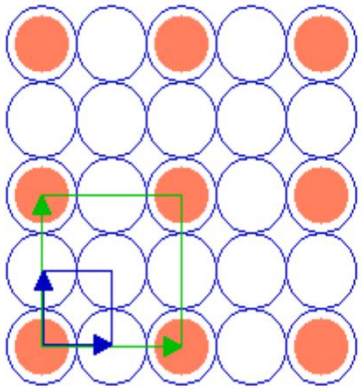


Substrate : fcc(111)
Substrate unit cell
Adsorbate unit cell



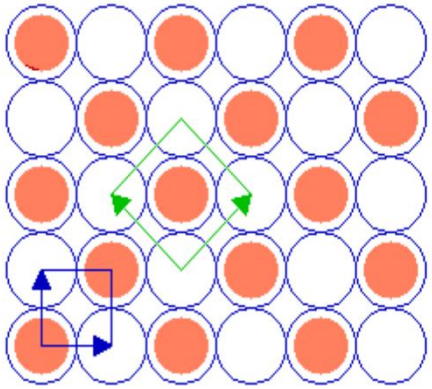
Substrate : fcc(111)
$(\sqrt{3} \times \sqrt{3})R30$

Adsorbovani sloj: matrična notacija



Substrate : fcc (100)
(2 x 2) overlayer

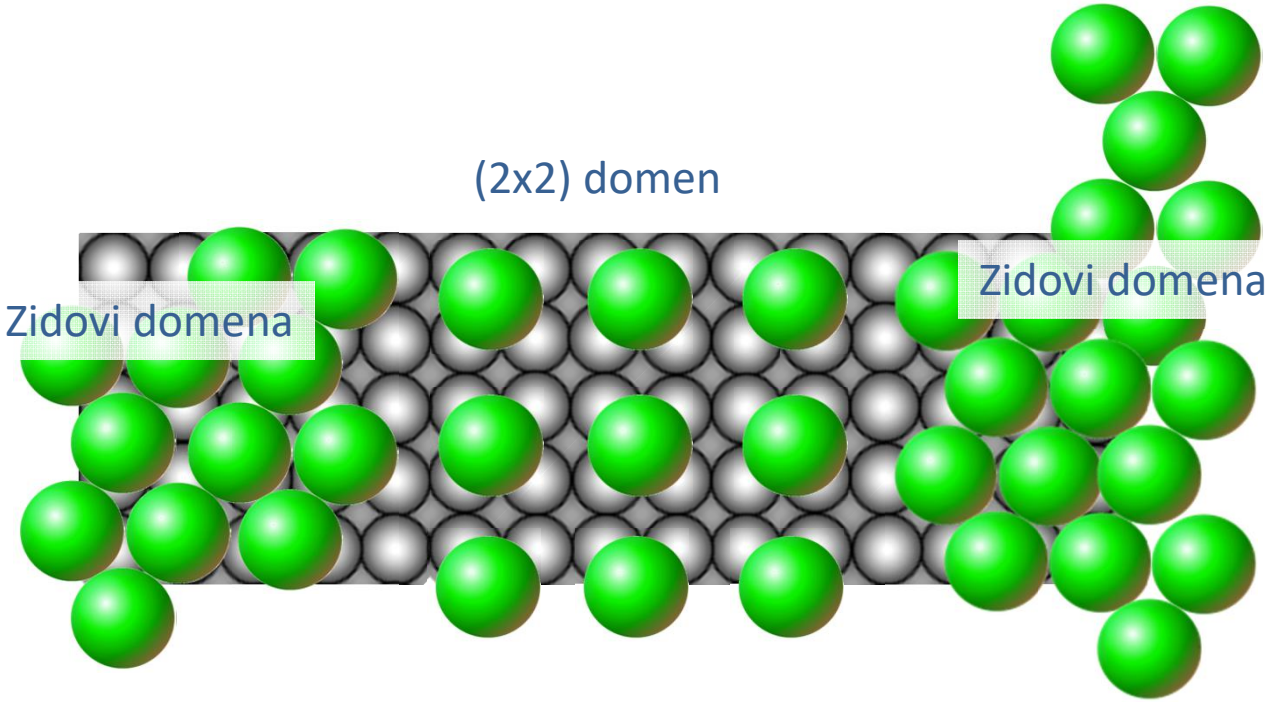
$$\begin{aligned} b_1 &= 2 \cdot a_1 + 0 \cdot a_2 \\ b_2 &= 0 \cdot a_1 + 2 \cdot a_2 \end{aligned} \quad \Rightarrow \quad M = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$$



Substrate : fcc (100)
c(2 x 2) overlayer

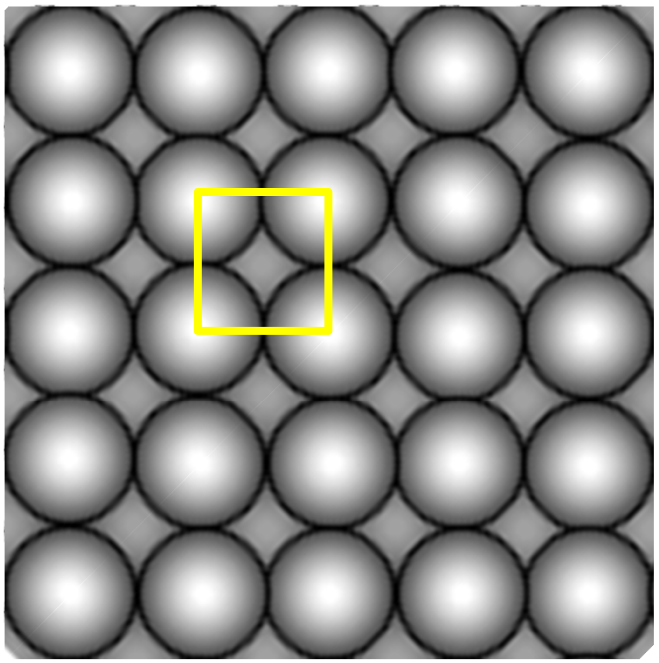
$$\begin{aligned} b_1 &= 1 \cdot a_1 + 1 \cdot a_2 \\ b_2 &= -1 \cdot a_1 + 1 \cdot a_2 \end{aligned} \quad \Rightarrow \quad M = \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}$$

Incommensurate Adsorption

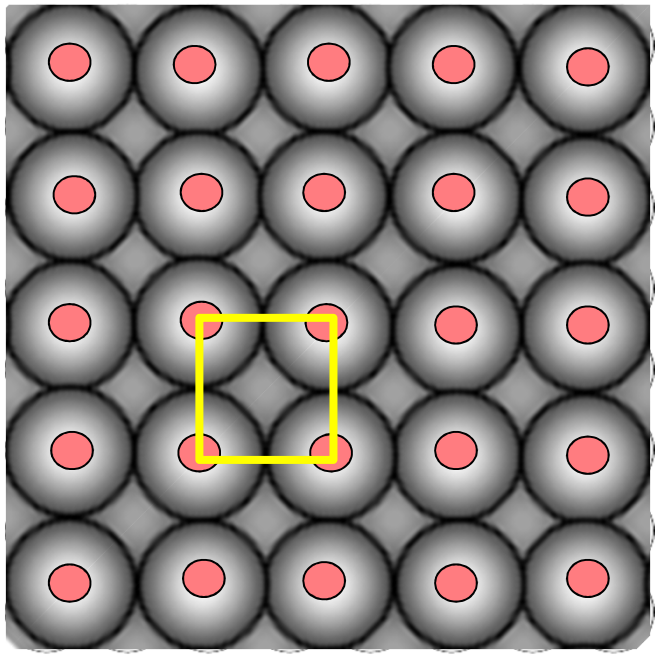


Persson et al. [1990].)

Kvadratna rešetka



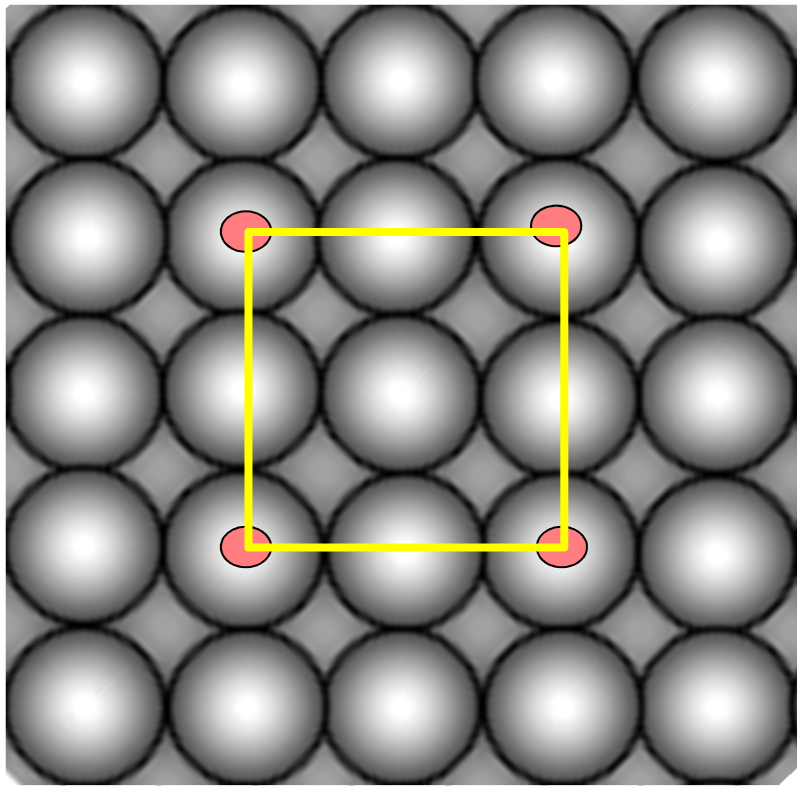
primitive unit cell



p(1x1)

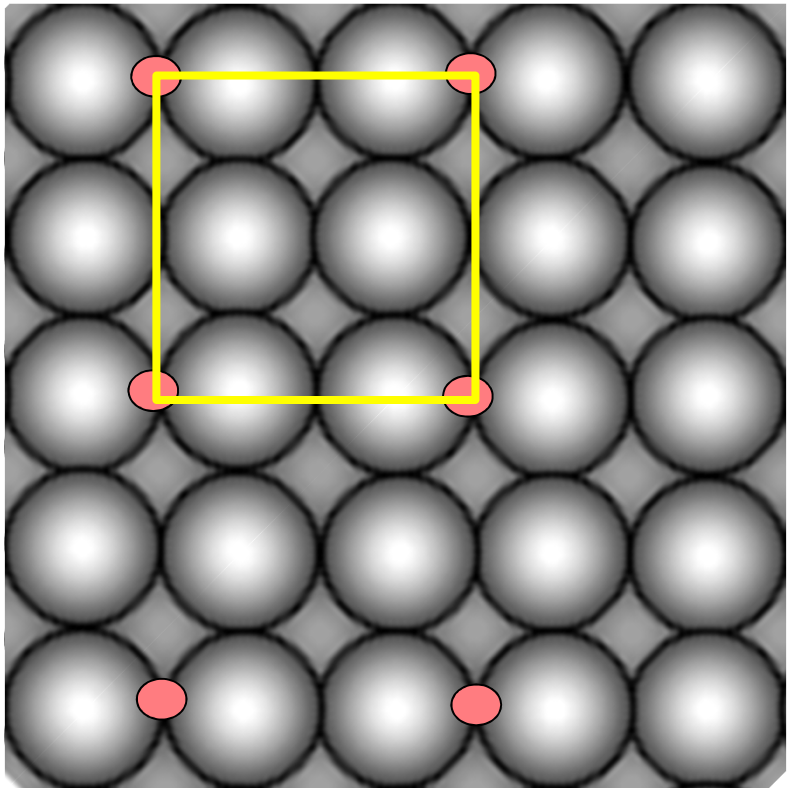
Kvadratna rešetka

c



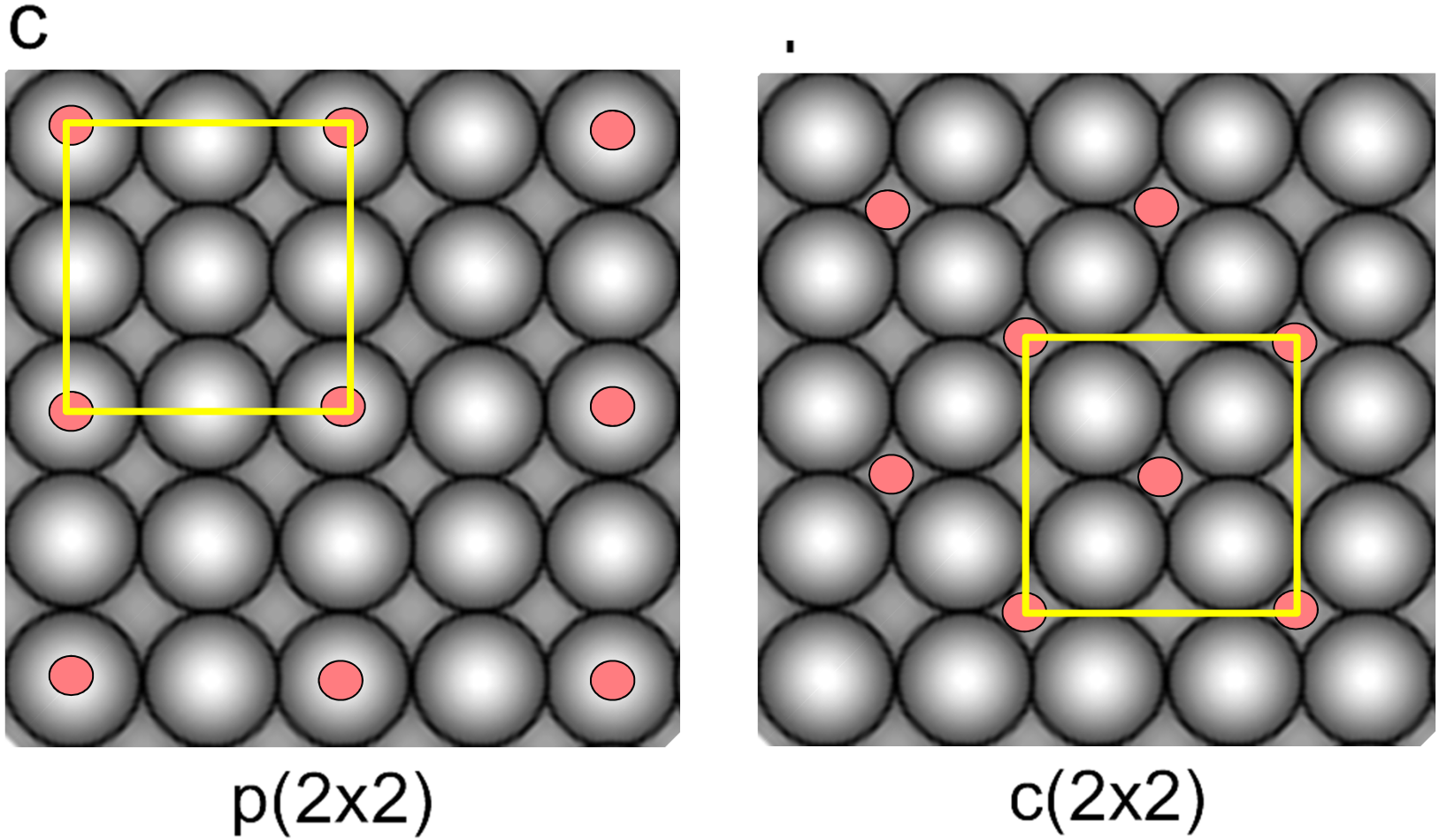
p(2x2)

d

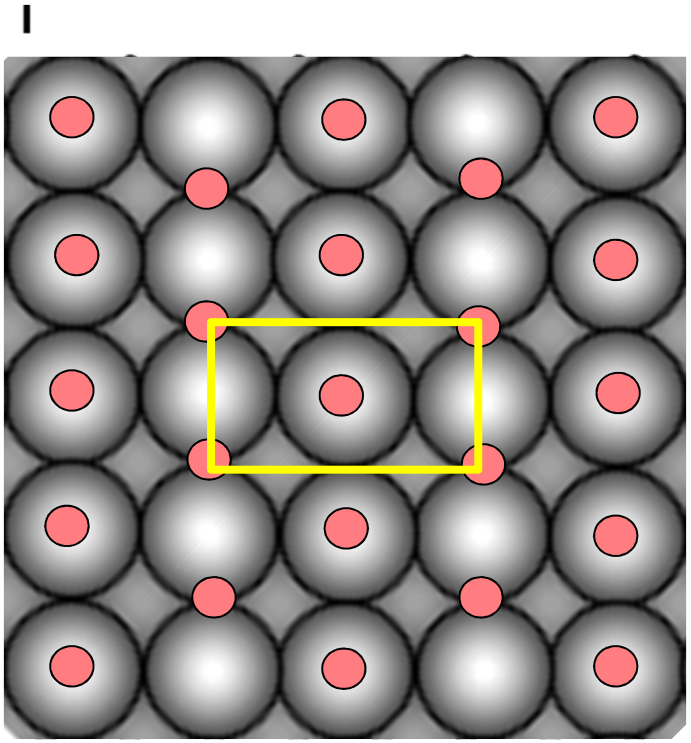


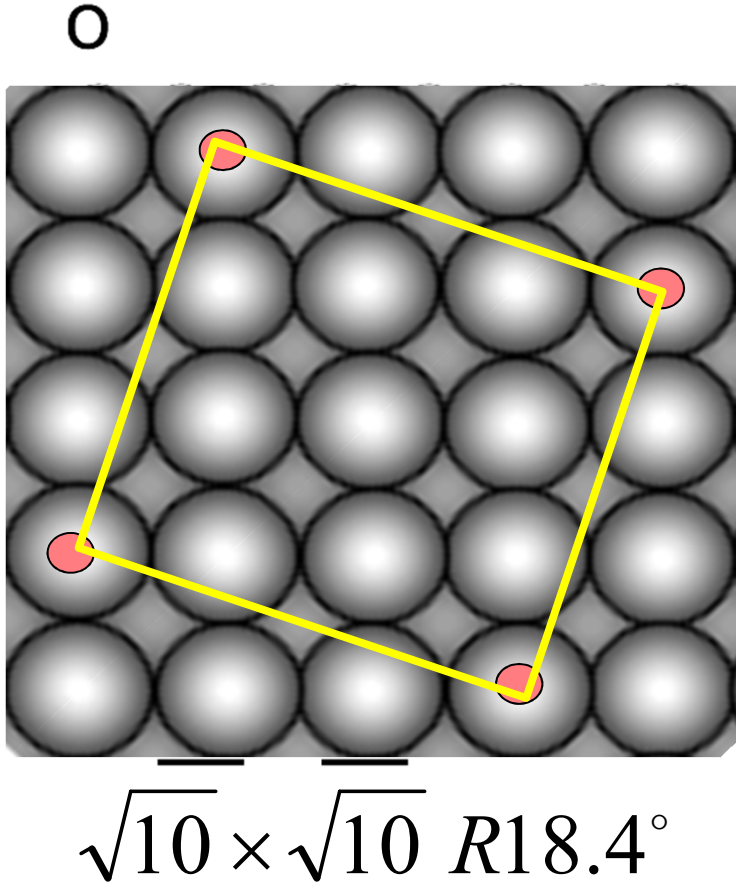
p(2x2)

Primitivna i centrirana rešetka



Kvadratna rešetka





$CH_3S/Au(111)$

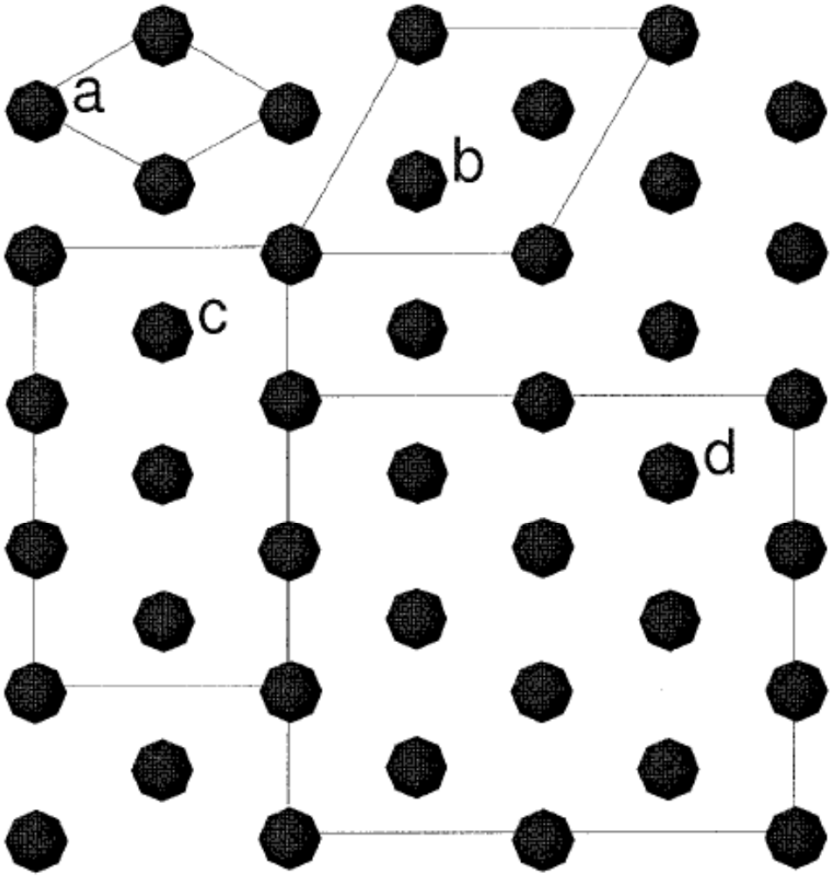
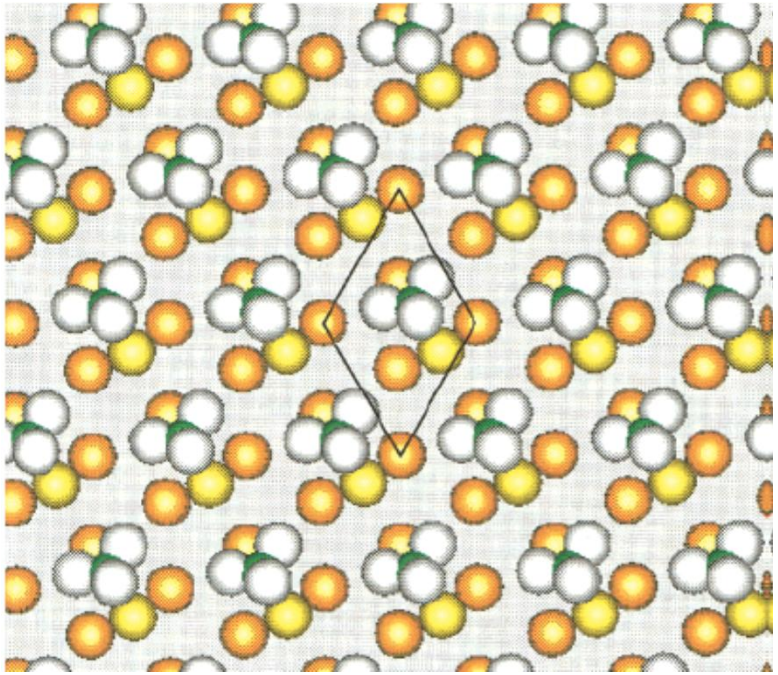
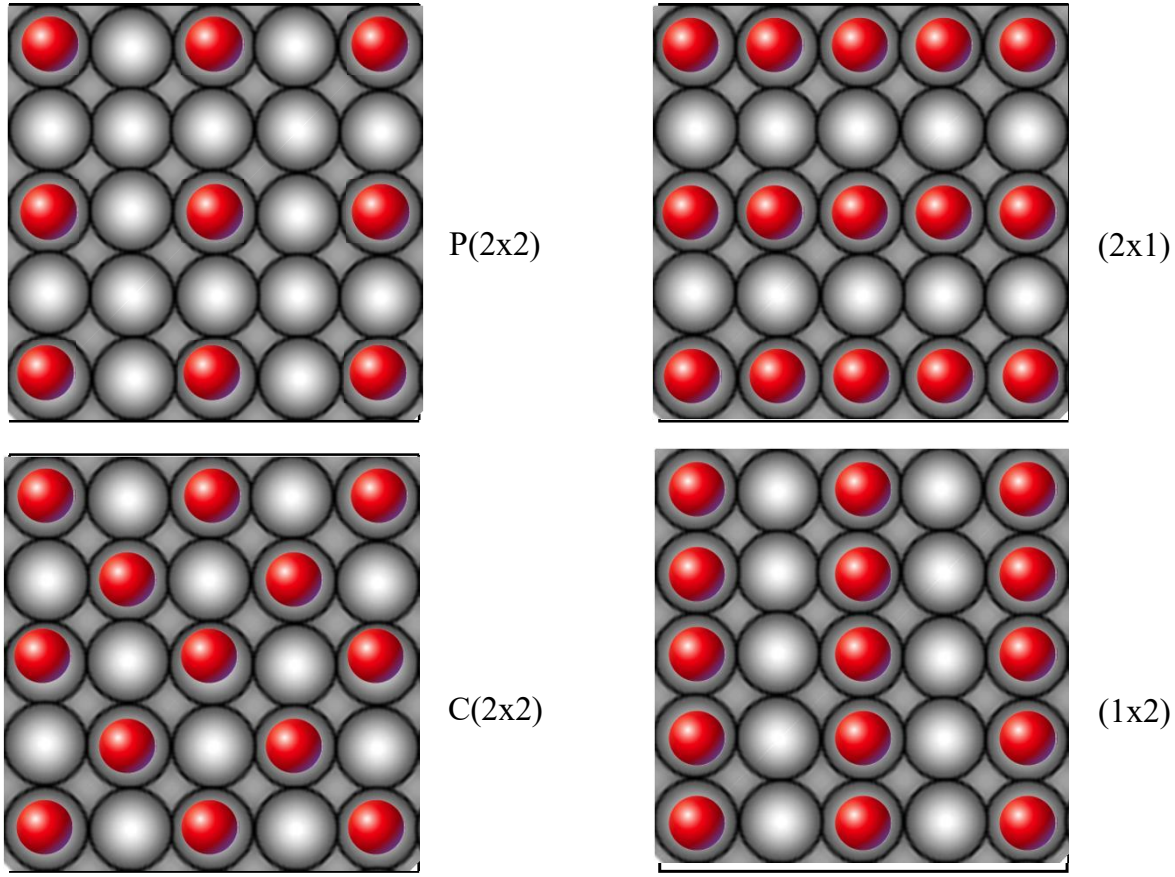


Figure 1. Surface cells used in the calculations. (a) (1 × 1); (b) ($\sqrt{3}\times\sqrt{3}$)R30; (c) (3 × $\sqrt{3}$); (d) (3 × 2 $\sqrt{3}$). These cells contain 1, 3, 6, and 12 Au atoms per layer, respectively. Cell d corresponds to the $c(4 \times 2)$ superlattice of the ($\sqrt{3} \times \sqrt{3}$)R30 lattice.

Θ	site	Δz	S−M	E_{ads}	cell
1	~on-top	2.84	3.00	4.4	*c*
1	~on-top	2.86	3.00	5.8	*d*
0.5	~on-top	2.84	2.98	5.9	*d*
1	fcc hollow	1.81	2.59	2.9	*b*
0.5	fcc hollow	1.60	2.51	11.5	*c*
0.25	fcc hollow	1.59	2.51	18.3	*d*
1	hcp hollow	1.90	2.60	−1.1	*b*
0.5	hcp hollow	1.70	2.53	4.7	*c*
1	bridge	2.09	2.52	18.6	*b*
0.5	bridge	2.07	2.50	19.6	*c*
0.25	bridge	2.05	2.49	21.8	*d*



Adsorpcija CO na kvadratnoj rešetki – adsorbovane faze



The absorption of molecules in a p(2x2), C(2x2), (2x1) overlayer. The dark circles represent sites, the red circles represent adsorption on the sites.

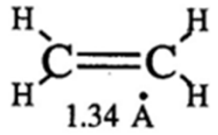
Hemisorpcija na metalima

- Metali imaju mnogo slobodnih elektrona koji učestvuju u vezivanju
- Veza je delokalizovana
- Elektroni su pokretni

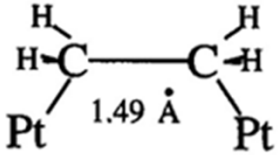
Adsorpcija je kompromis – da bude dobro i adsorbatu i substratu

Mehanizam aktivacije hemijske veze u katalizi

Gaseous Benzene

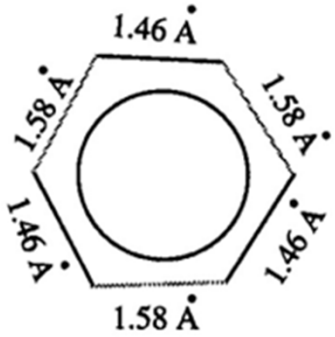


Gaseous Ethylene

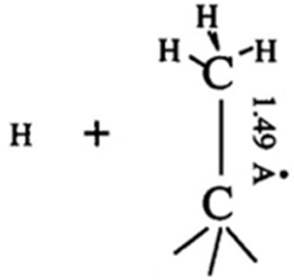


Ethylene On 100 K Pt(111)

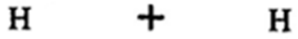
Gaseous Hydrogen



(3x3) Benzene On Rh(111)

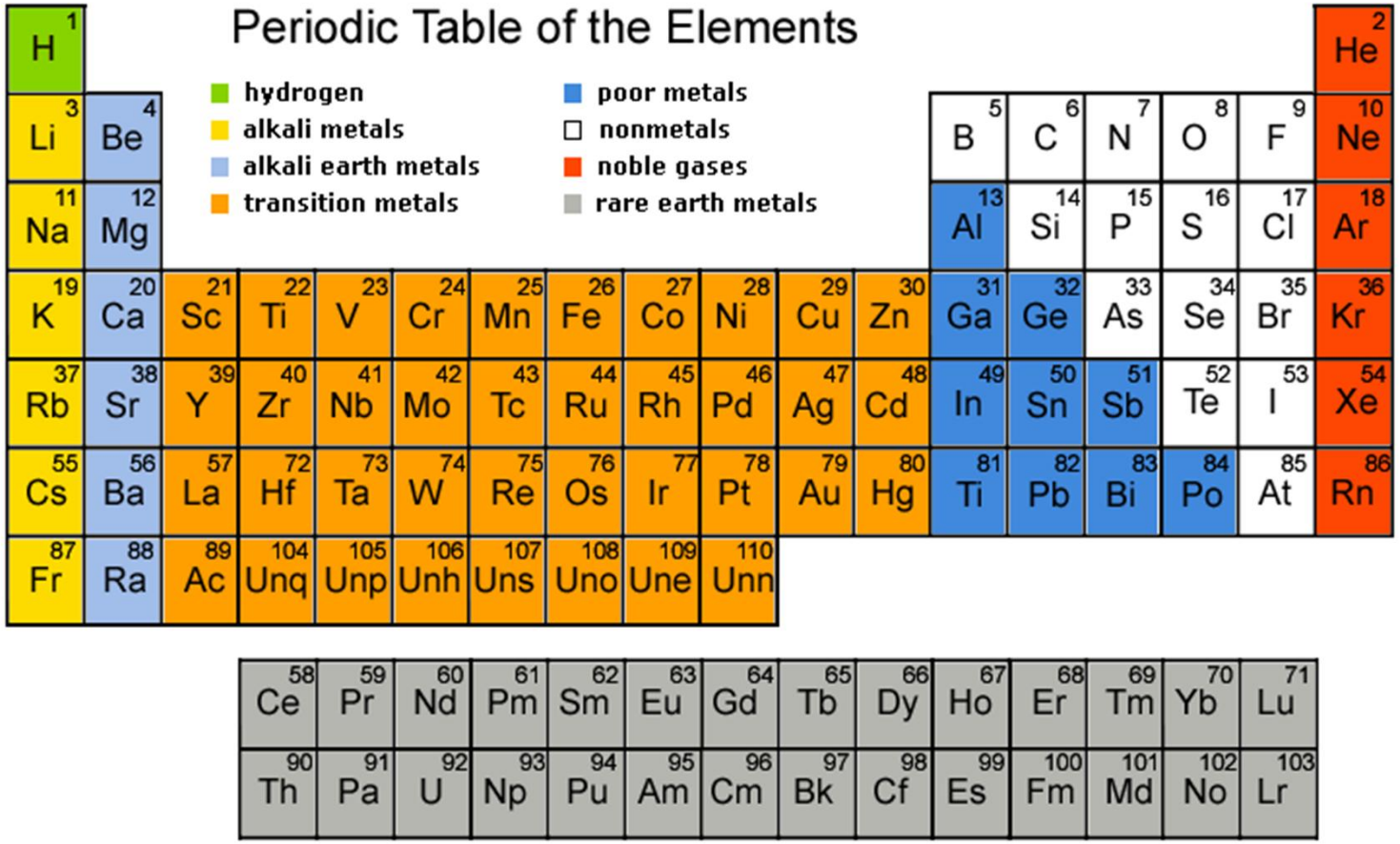


Ethylene On 300 K Pt(111)



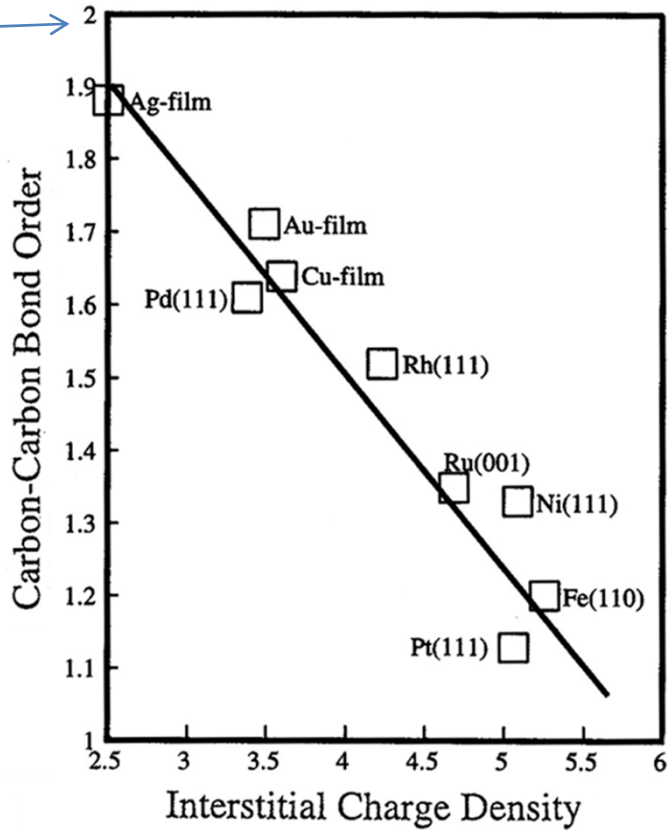
Hydrogen On Platinum

Trendovi u periodnom sistemu



Često dobra korelacija između elektronske gustine, elektronegativnosti i adsorpcionih svojstava

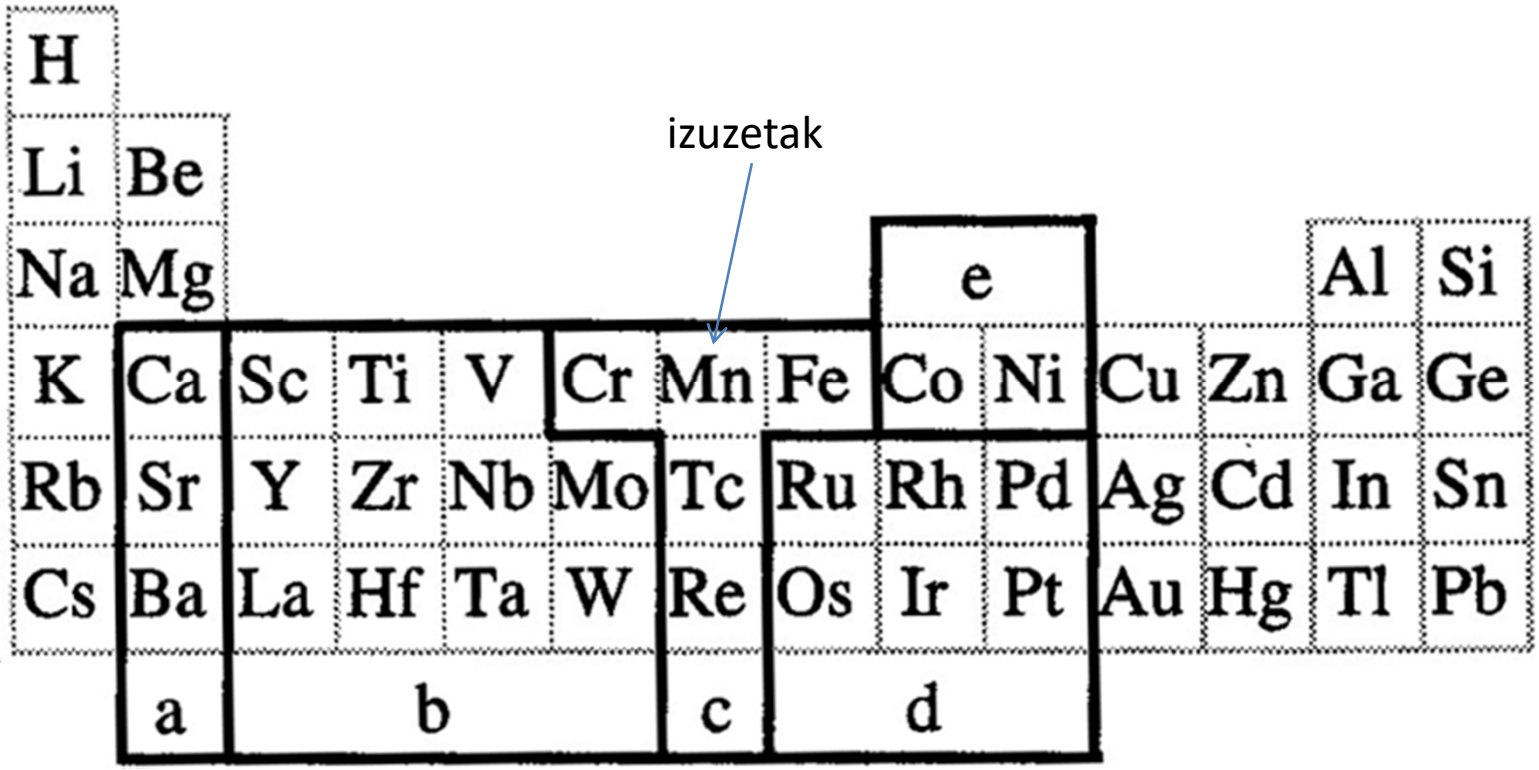
Etilen u gasnoj fazi



Red C-C veze u adsorbovanom etilenu

Sigma veze

Adsorpcija kroz periodni sistem

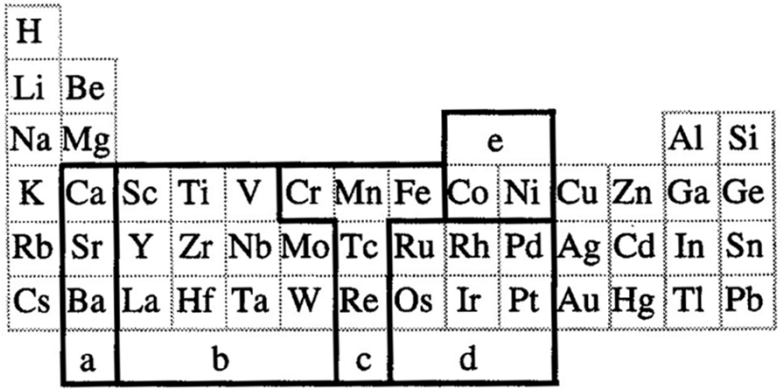


Klasifikacija prema reaktivnosti površine

Slično se ponašaju površine metala koji imaju slične elektronske gustine i elektronegativnosti

Kvalitativni aspekti

	Adsorbing Gas			
Metal	H_2	O_2	N_2	CO
Group a	2 or 3	3	2	3
Group b	3	3	3	3
Group c	3	3	2	3
Group d	3	3	2	3
Group e	3	3	2	3
Cu	2	3	2	1
Ag	0	2 or 3	0	0
Au	0	0	0	3
Al	0	*def*-3	0	3
K, Na, Li	0	3	0	0

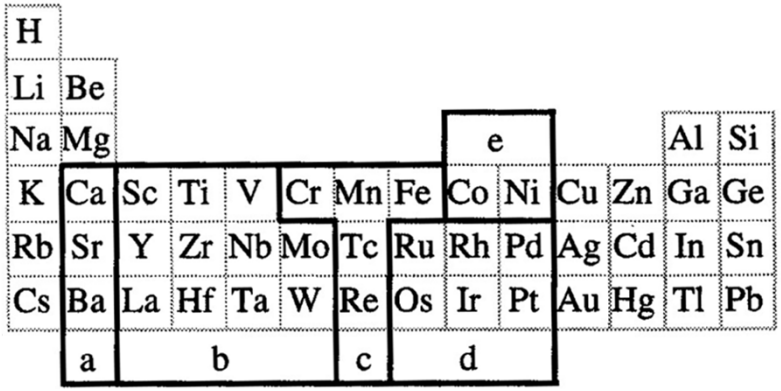


Nedovoljna elektronska gustina

0 – nema adsorpcije
1 – ima na 100 K ali nema na 300 K
2 – aktivirani proces
3 – brza adsorpcija na sobnoj temperaturi

Kvalitativni aspekti

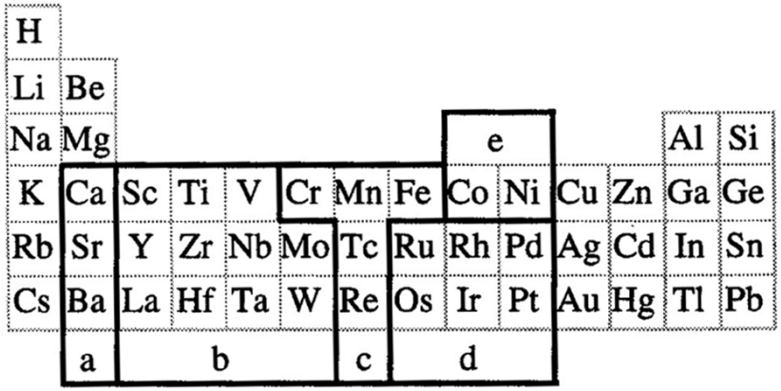
	Adsorbing Gas			
Metal	H_2	O_2	N_2	CO
Si, Ge	0 or 2	3	0	0
InP	0	3	0	0
NiO	0	1		
ZnO	*def*-3	*def*-3	?	1
MgO				
Al_2O_3	0	1		
SiO_2	*def*-2	*def*-3		
NaCl	*0*	*?*	1	0-100K
LiF				1-40 K



0 – nema adsorpcije
1 – ima na 100 K ali nema na 300 K
2 – aktivirani proces
3 – brza adsorpcija na sobnoj temperaturi

Kvalitativni aspekti

Metal	C_2H_2 C_2H_4	CH_4 C_2H_6	CH_3OH	H_2O
Group a	3	?	?	3
Group b	3	2	3	?
Group c	3	?	3	1
Group d	3	2	3	1
Group e	3	2	3	1
Cu	1 or 3	0	1	1
Ag	1	0	1	1
Au	3	0	1	1
Al	2	?	3	3
K, Na, Li	3 C_2H_2 0 C_2H_4	?	?	3

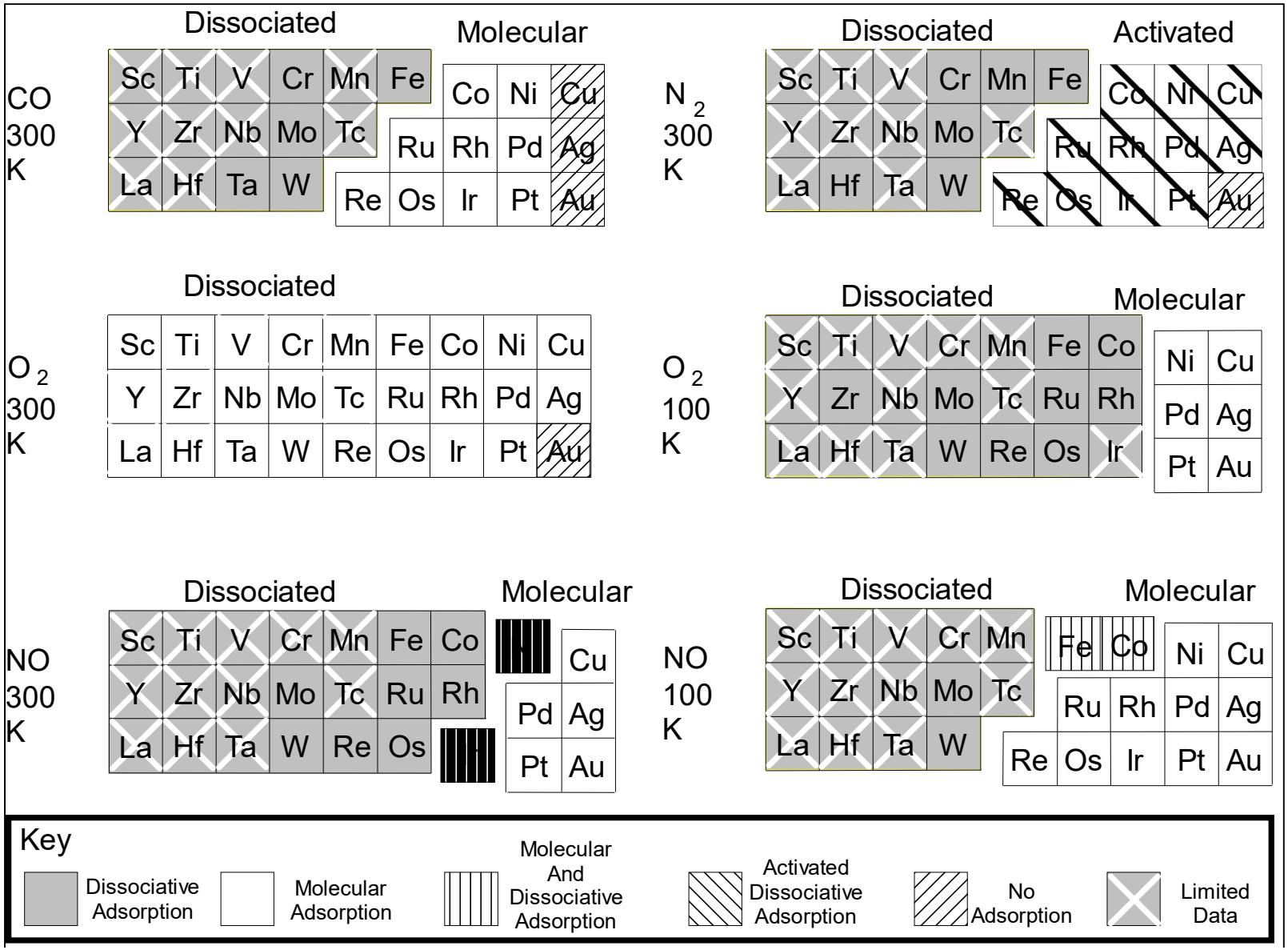


0 – nema adsorpcije
1 – ima na 100 K ali nema na 300 K
2 – aktivirani proces
3 – brza adsorpcija na sobnoj temperaturi

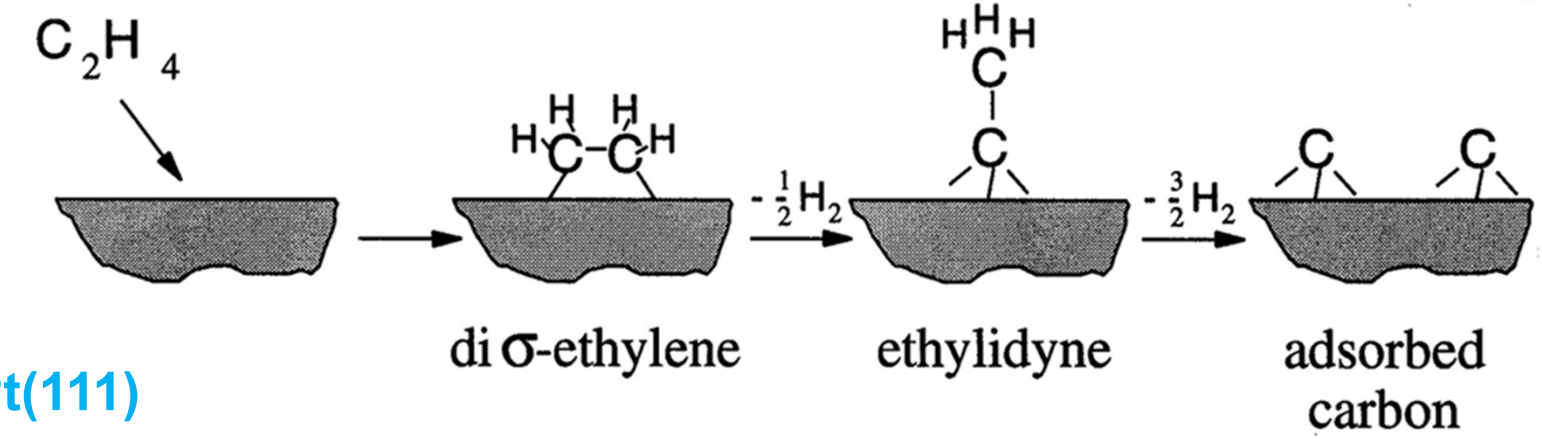
Molekulska i disocijativna adsorpcija

Brodén et al. [1976]

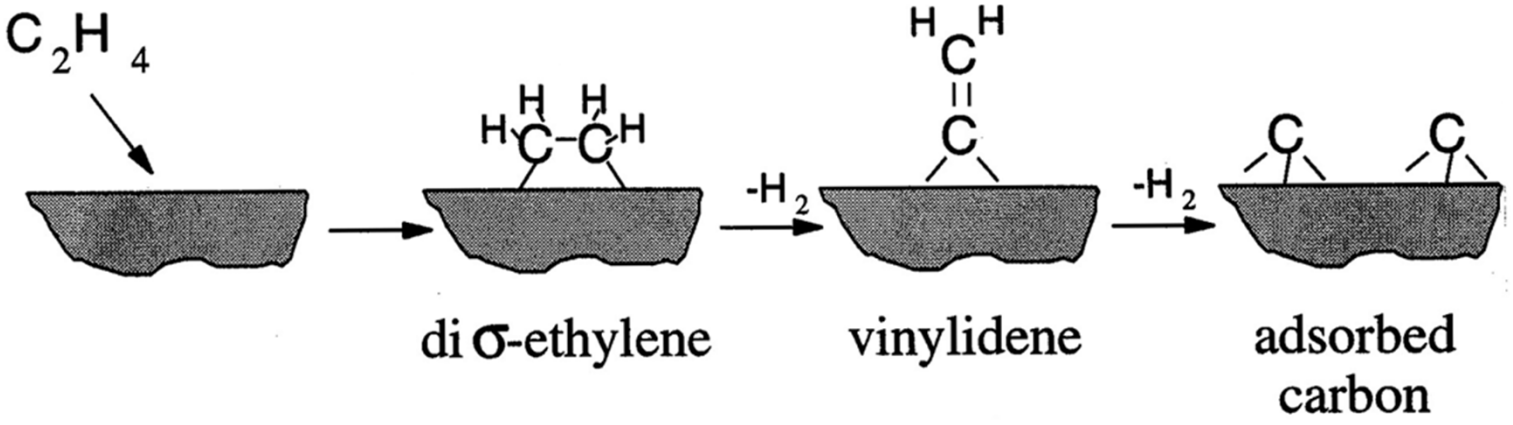
10^{-6} torr



Strukturna osetljivost



Pt(111)



(1x1)Pt(100)

Različite klase adsorbata na metalnim površinama

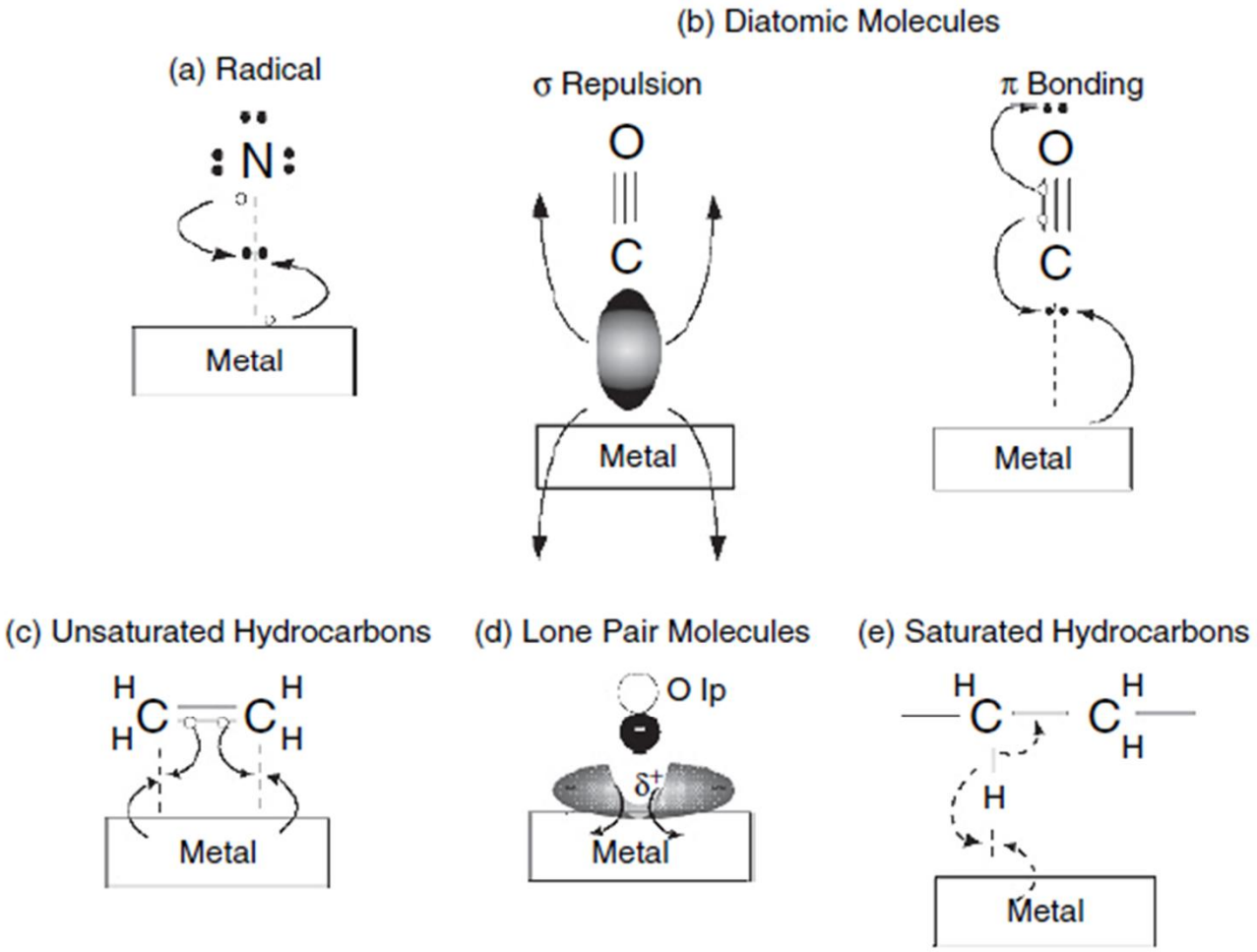
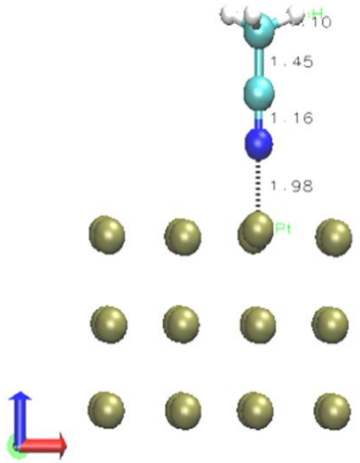
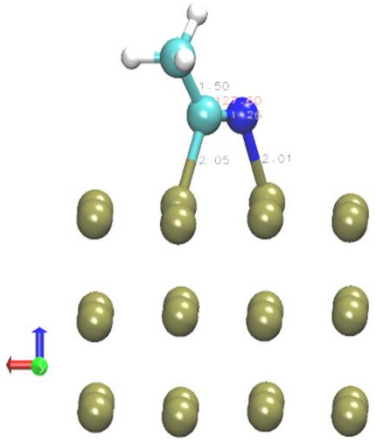


Figure 2.58. Schematic illustrations of the five different types of chemical bond formation on metal surfaces.

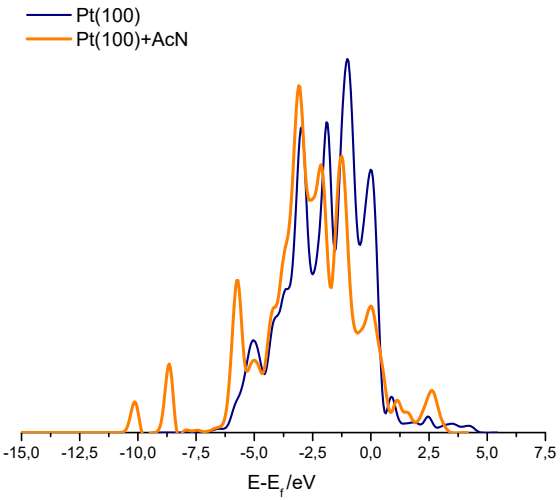
Primer: AcN na Pt(001)

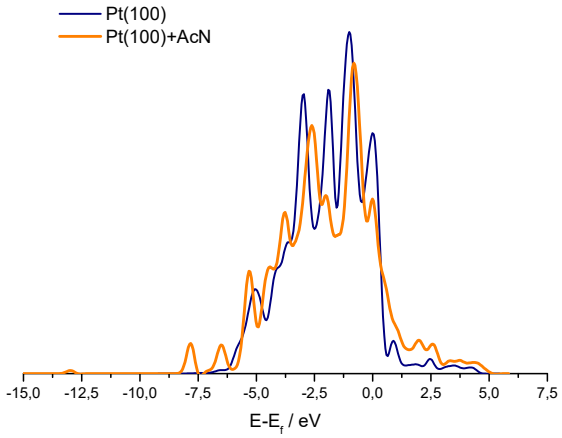


-0,79 eV



-1,24 eV





Korelacija sa elektronskom strukturom

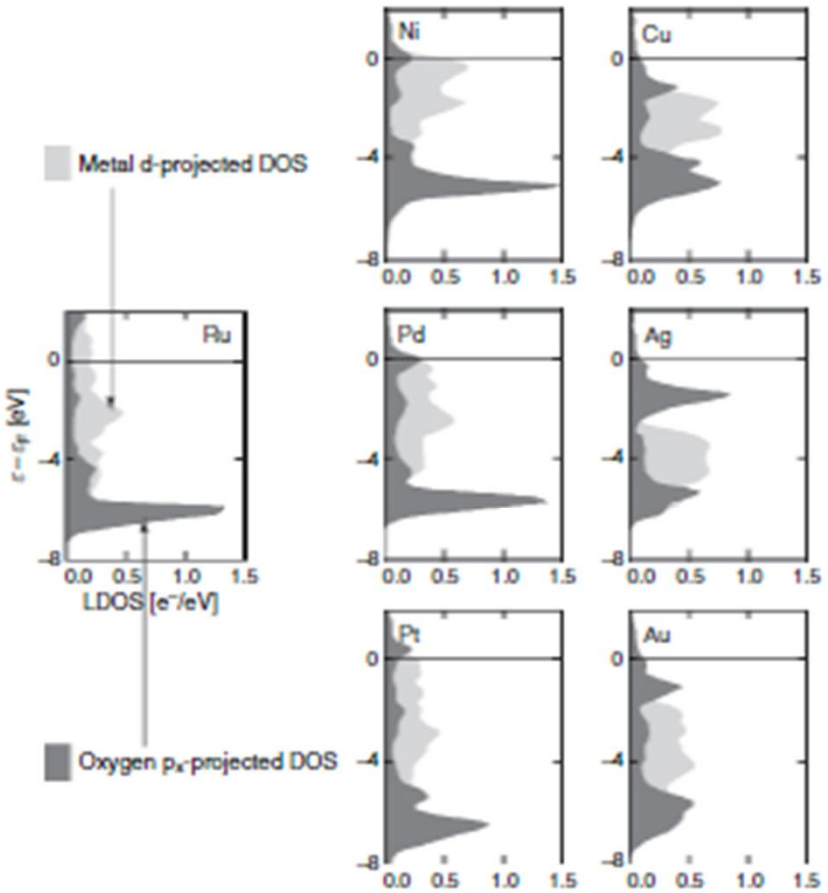


Figure 4.2. The density of states projected onto the d states of the surface atoms for the surfaces considered in Figure 4.1 (grey). Also shown (black) is the oxygen $2p_x$ projected density of states for O adsorbed on the same surfaces. The formation of bonding and anti-bonding states below and above the metal d states is clearly seen. Adapted from Ref. [4].

Korelacija sa elektronskom strukturom

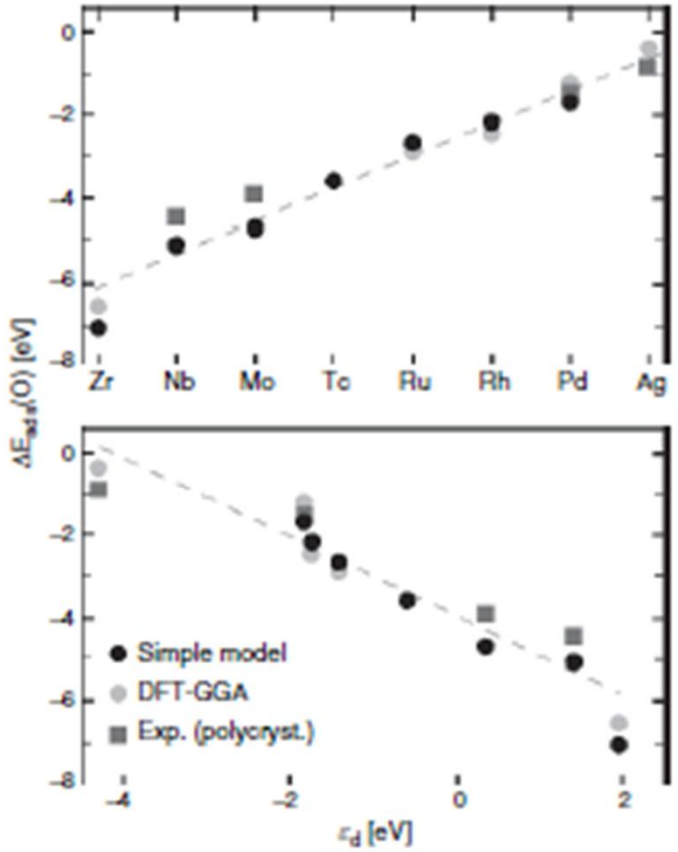
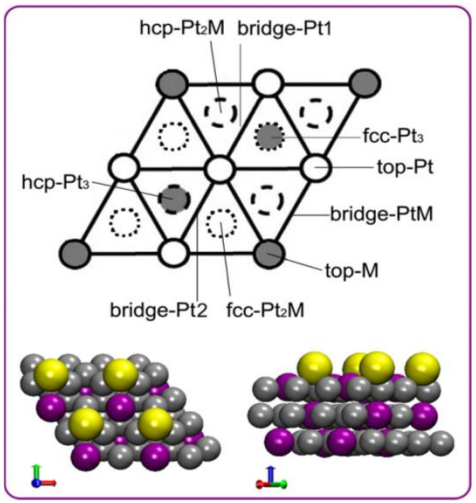
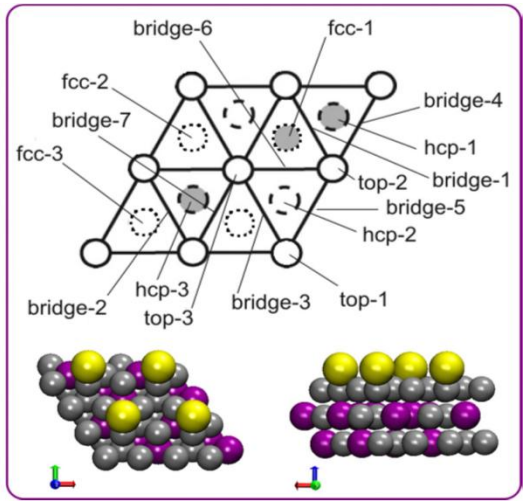


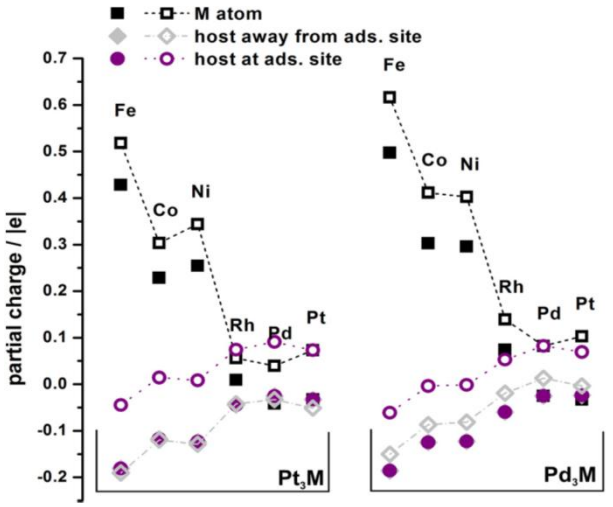
Figure 4.6. Variations in the O adsorption energy along the 4d transition metal series. The results of full DFT calculations are compared to those from the simple d band model and to experiments. Below the same data are plotted as a function of the d band center. Adapted from Ref. [4].

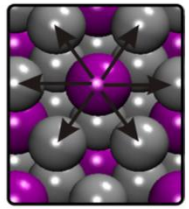
Energije adsorpcije mnogih jednostavnih adsorbata se korelišu sa centrom d-trake metalnog subtrata

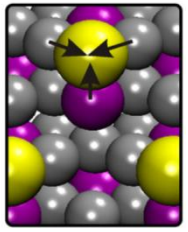
Korelacija sa elektronskom strukturom

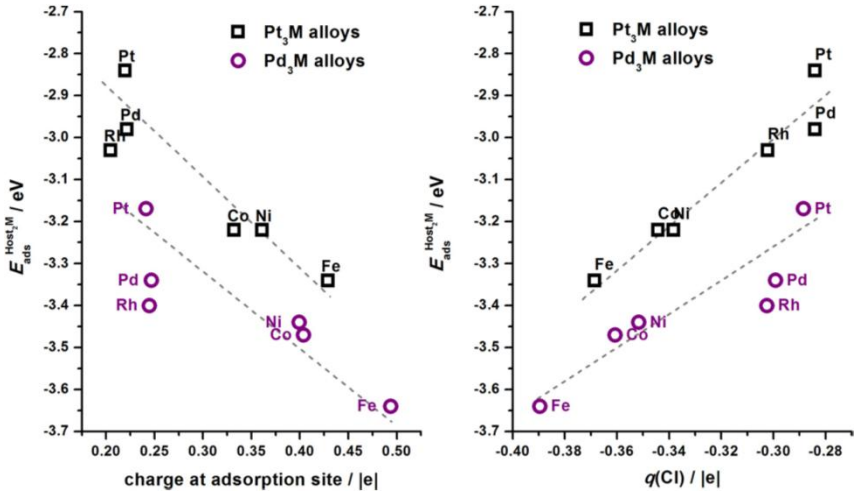












Electrochimica Acta 130 (2014) 453–463

Energije adsorpcije mnogih jednostavnih adsorbata se korelišu sa centrom d-trake metalnog subtrata

Korelacija sa elektronskom strukturom

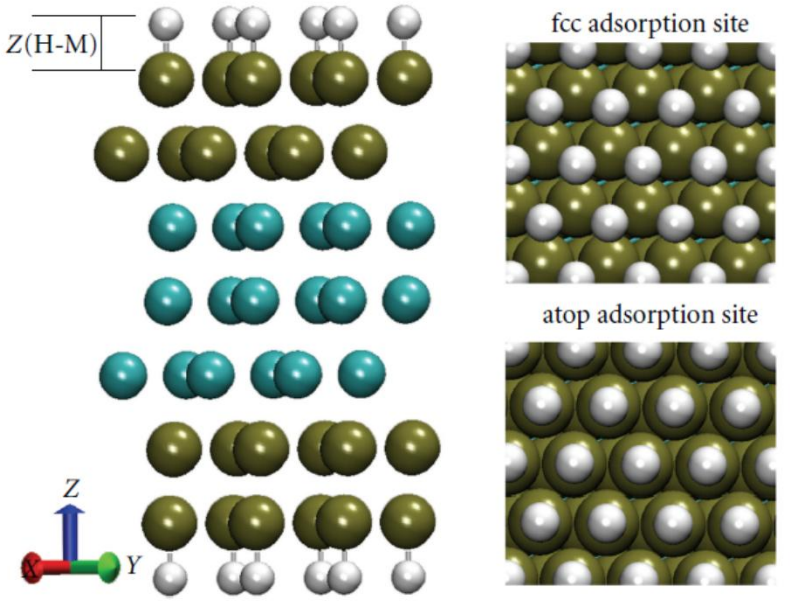


FIGURE 1: A side view of the metal slabs applied for hydrogen adsorption analysis and a perpendicular view of the surface covered with hydrogen adsorbed on fcc and atop site. For graphical representations, Visual Molecular Dynamics was used [22].

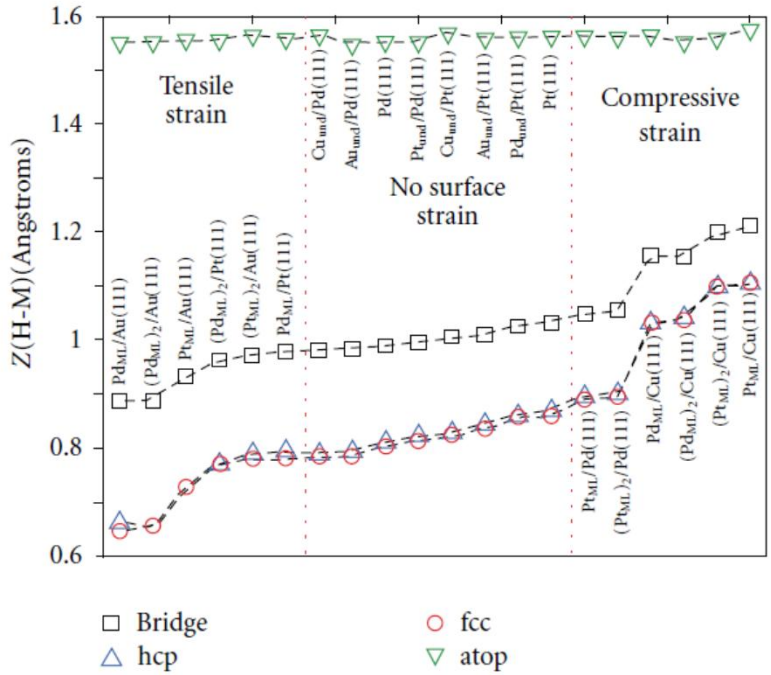


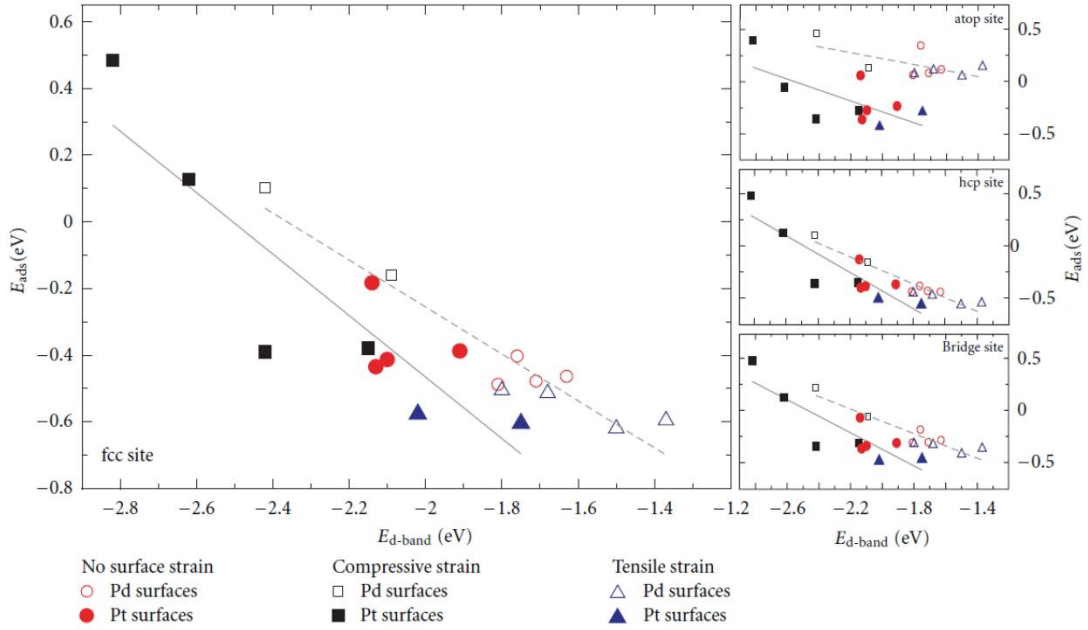
FIGURE 2: Calculated values of Z(H-M) on fcc (circles), hcp (up triangles), atop (down triangles), and bridge sites (squares).

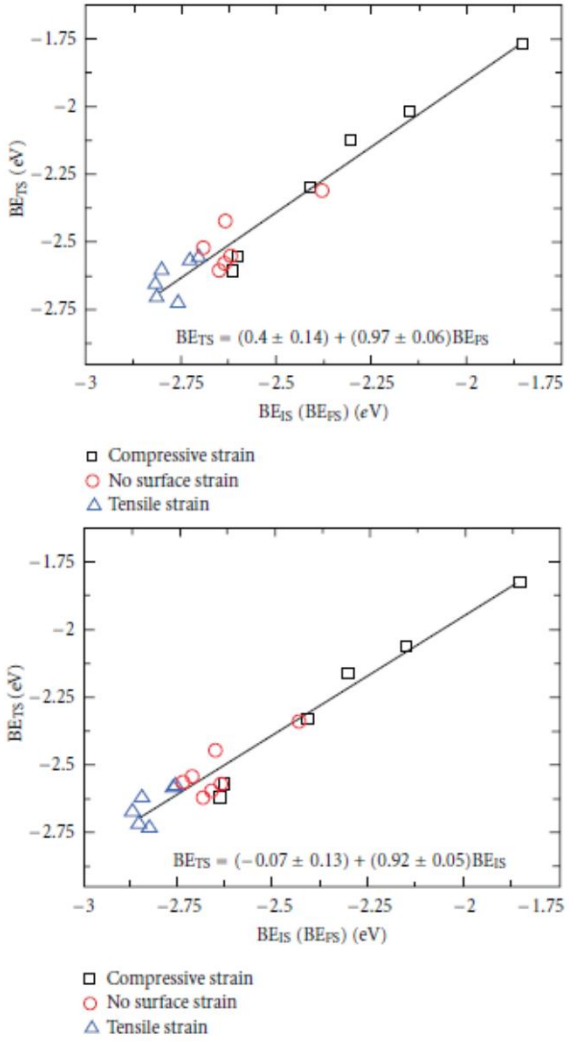
Advances in Physical Chemistry
Volume 2011, Article ID 305634, 8 pages
doi:10.1155/2011/305634

Energije adsorpcije mnogih jednostavnih adsorbata se korelišu sa centrom d-trake metalnog subtrata

Korelacija sa elektronskom strukturom

Adsorpcija i mobilnost adsorbata





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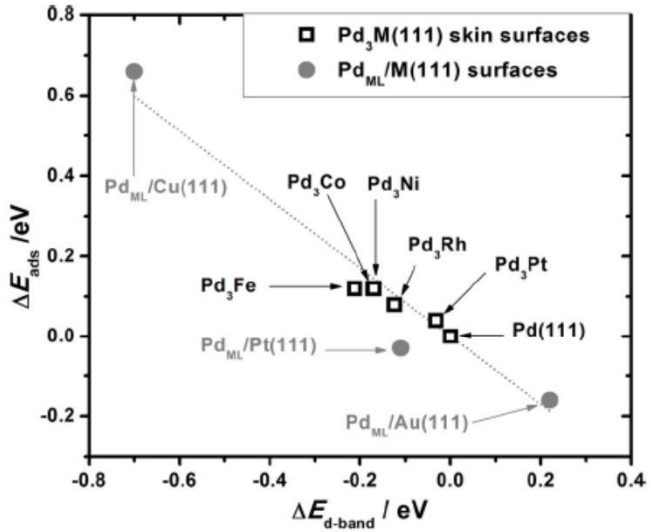
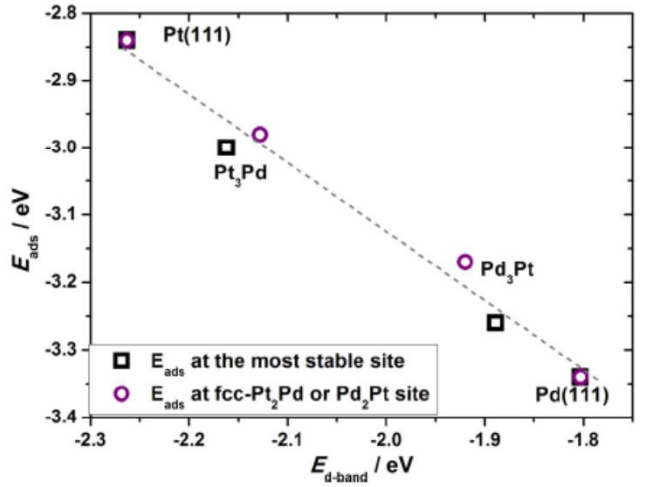
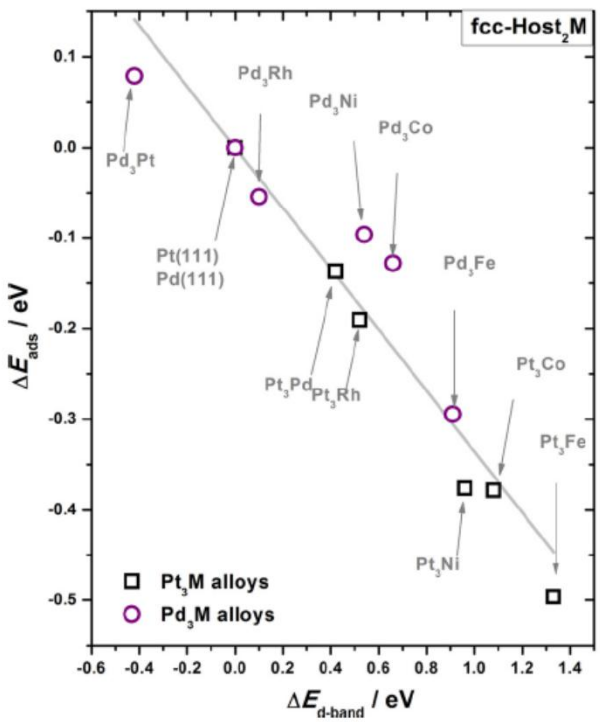
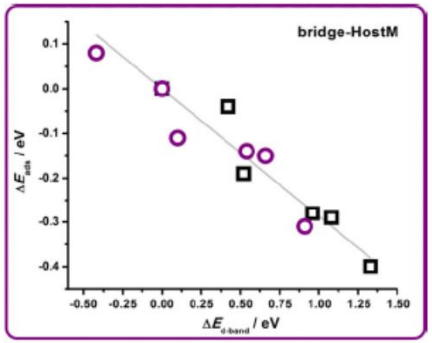
Energije adsorpcije mnogih jednostavnih adsorbata se korelišu sa centrom d-trake metalnog subtrata

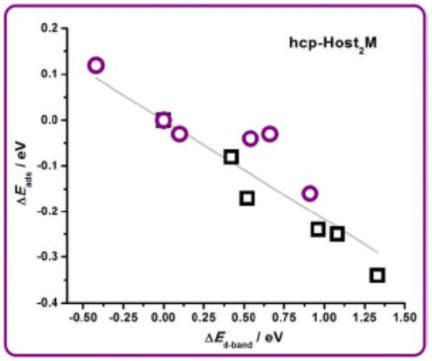
Korelacija sa elektronskom strukturom







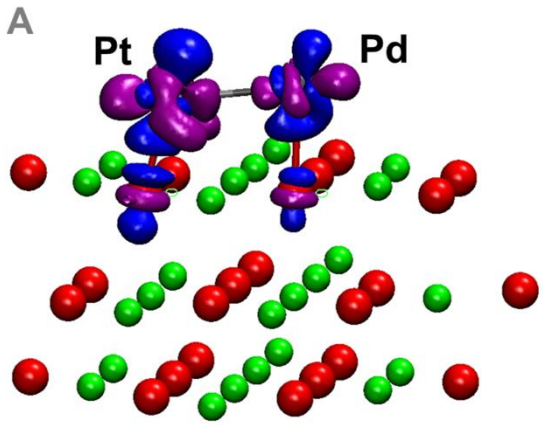




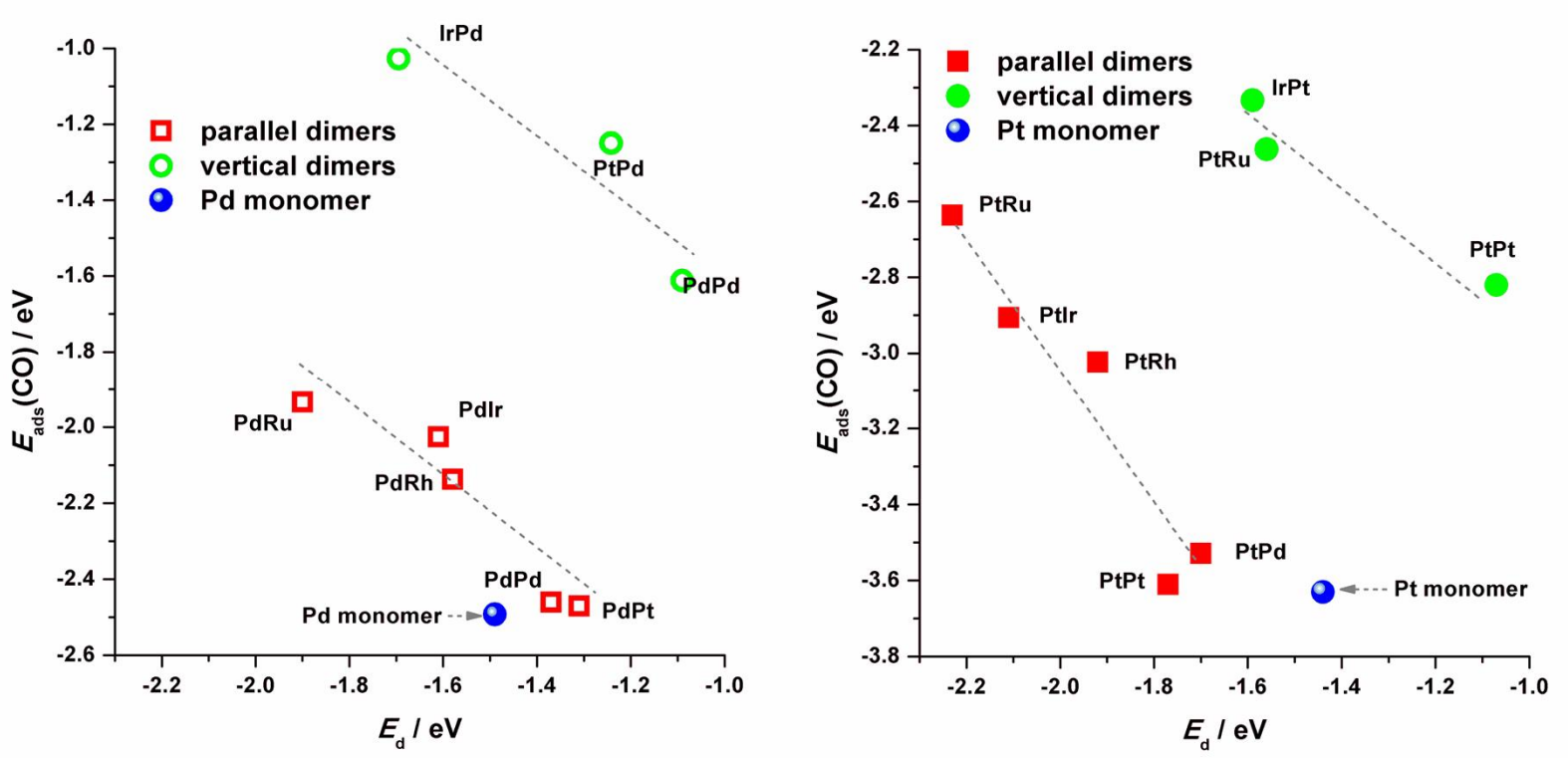
Electrochimica Acta 130 (2014) 453–463

Energije adsorpcije mnogih jednostavnih adsorbata se korelišu sa centrom d-trake metalnog subtrata

Adsorpcija na nisko-koordinisanim metalnim atomima
(defekti, kinkovi, stepenice, adsorbovani klasteri – katalizatori!)

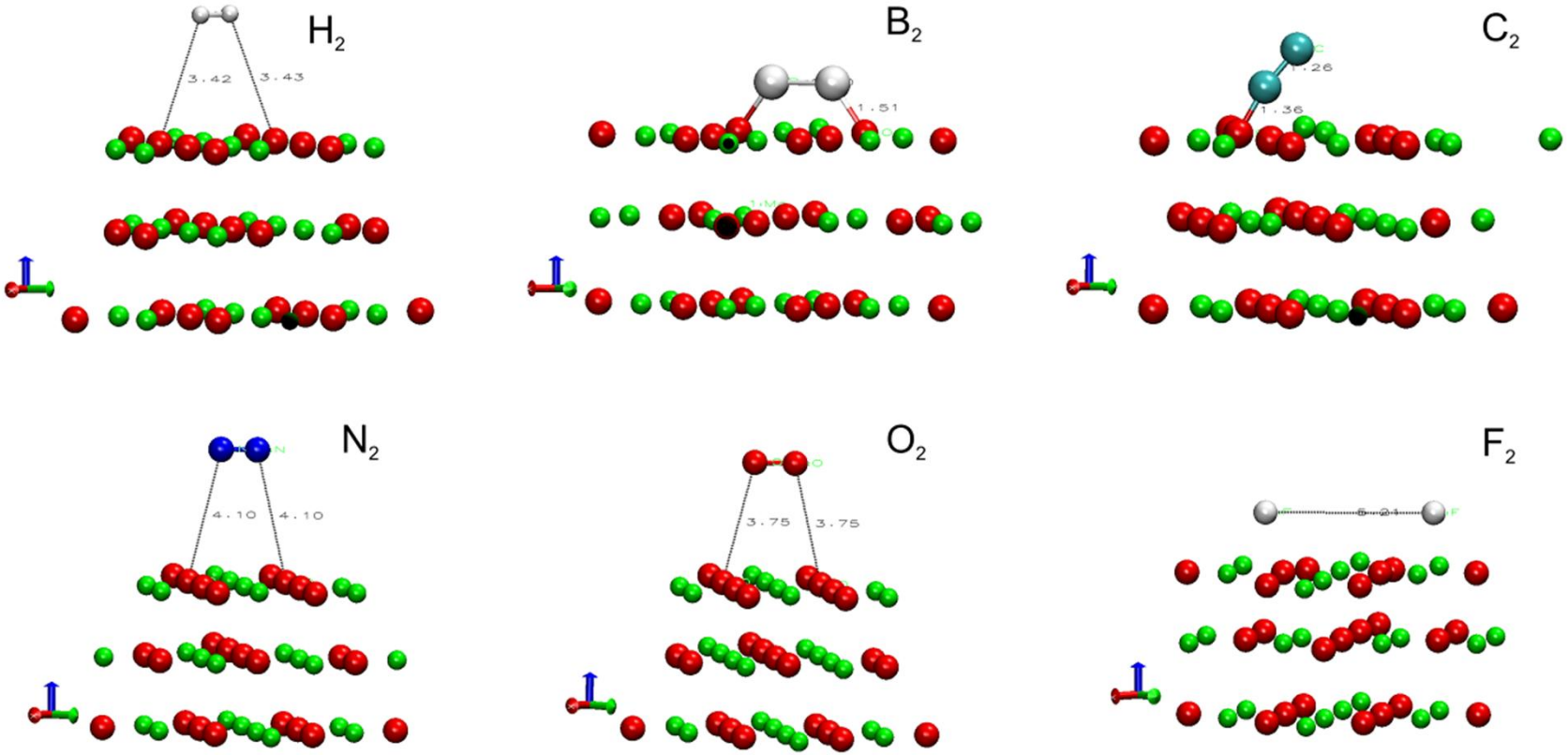


Nema jedinstvene teorije

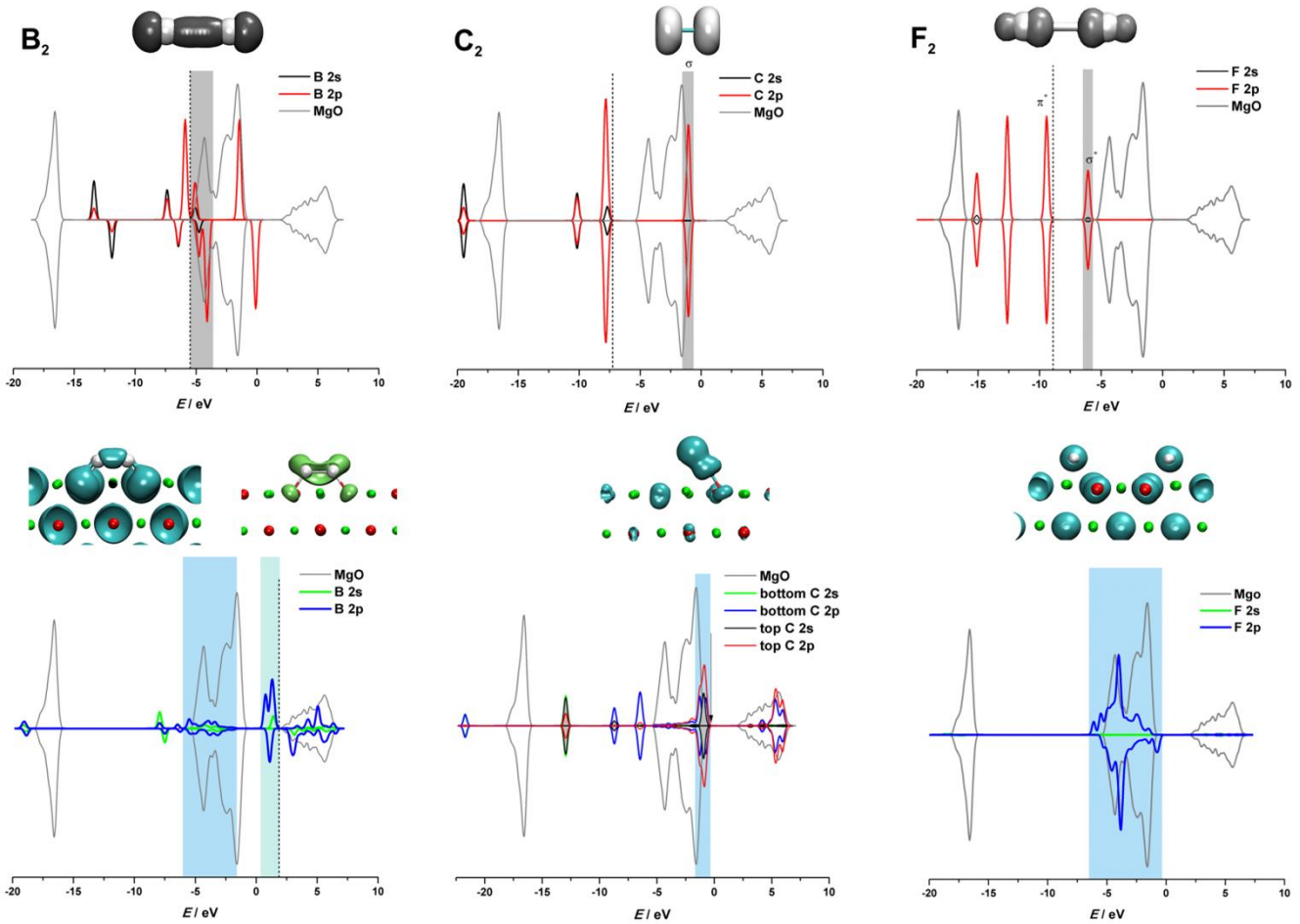


Adsorpcija na oksidima – nema jedinstvene teorije
Primer: X_2@MgO(001)

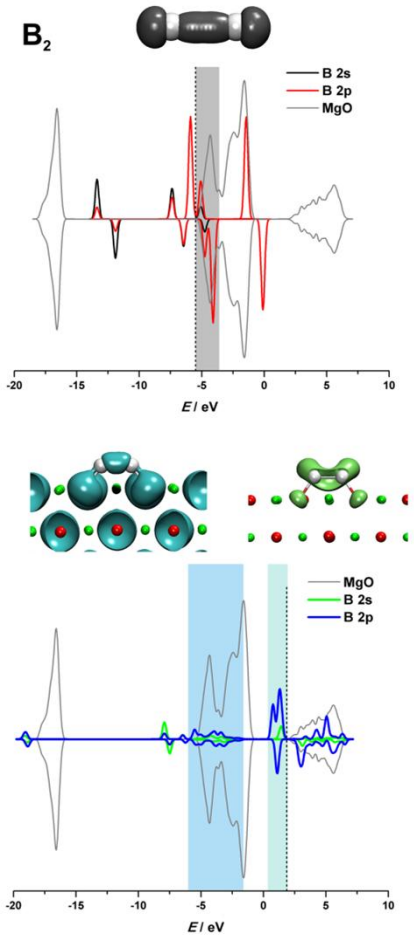
Svojstva jonskih kristala!!!

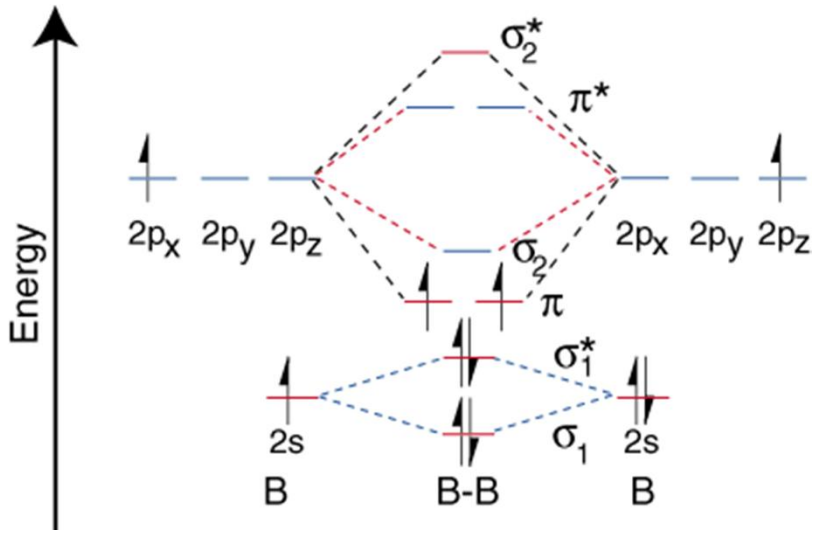


Adsorpcija na oksidima – nema jedinstvene teorije
Primer: C_2@MgO(001)

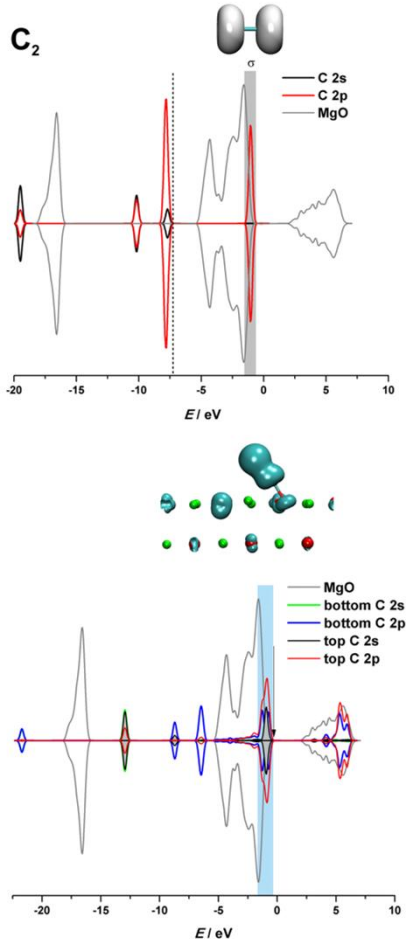


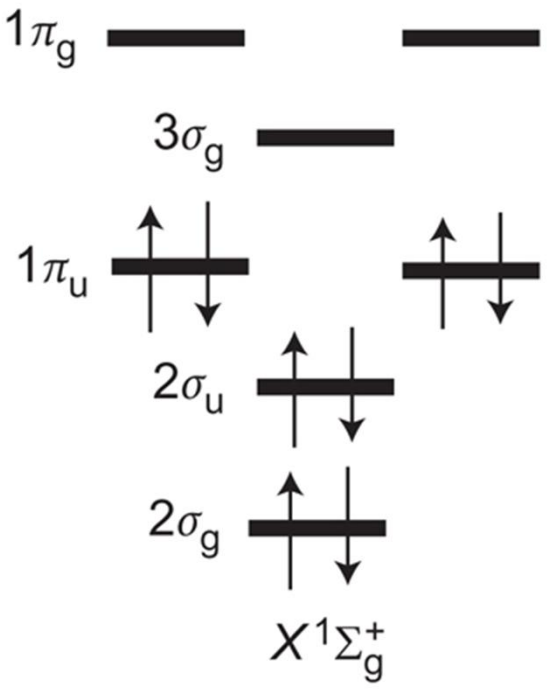
Adsorpcija na oksidima – nema jedinstvene teorije
Primer: B_2@MgO(001)



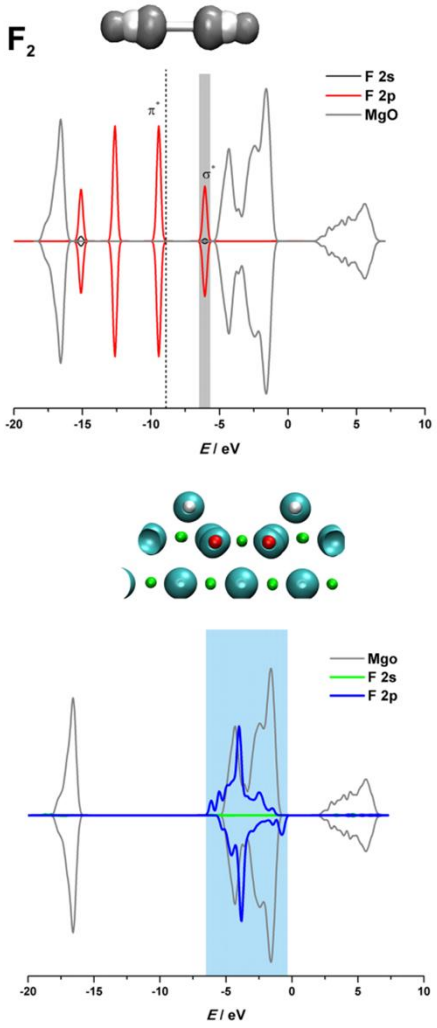


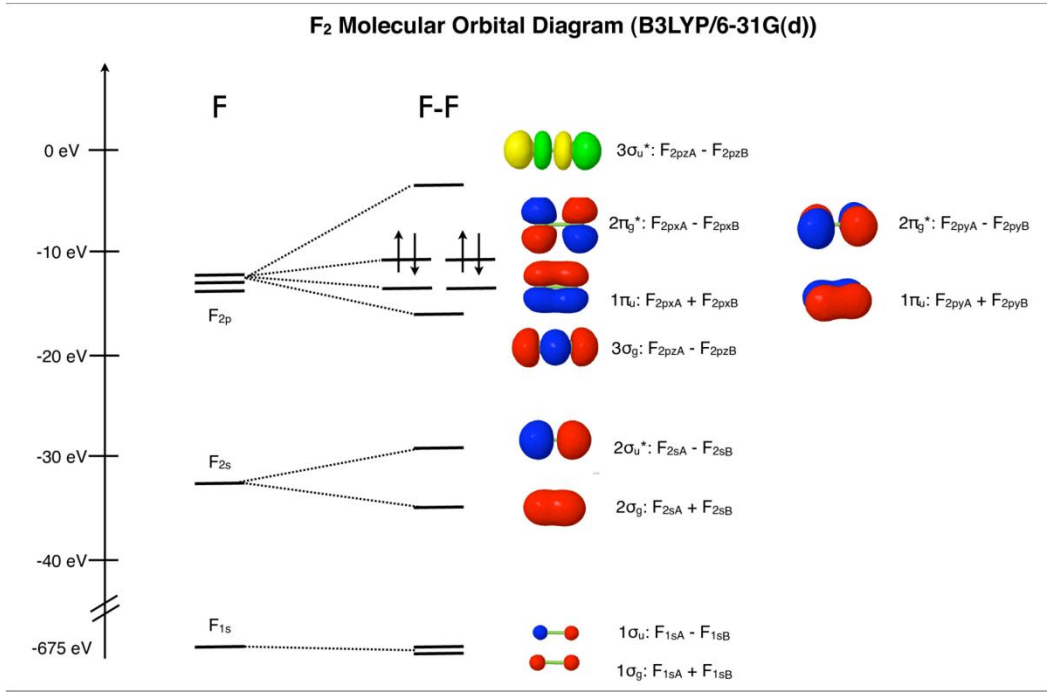
Adsorpcija na oksidima – nema jedinstvene teorije
Primer: C_2@MgO(001)



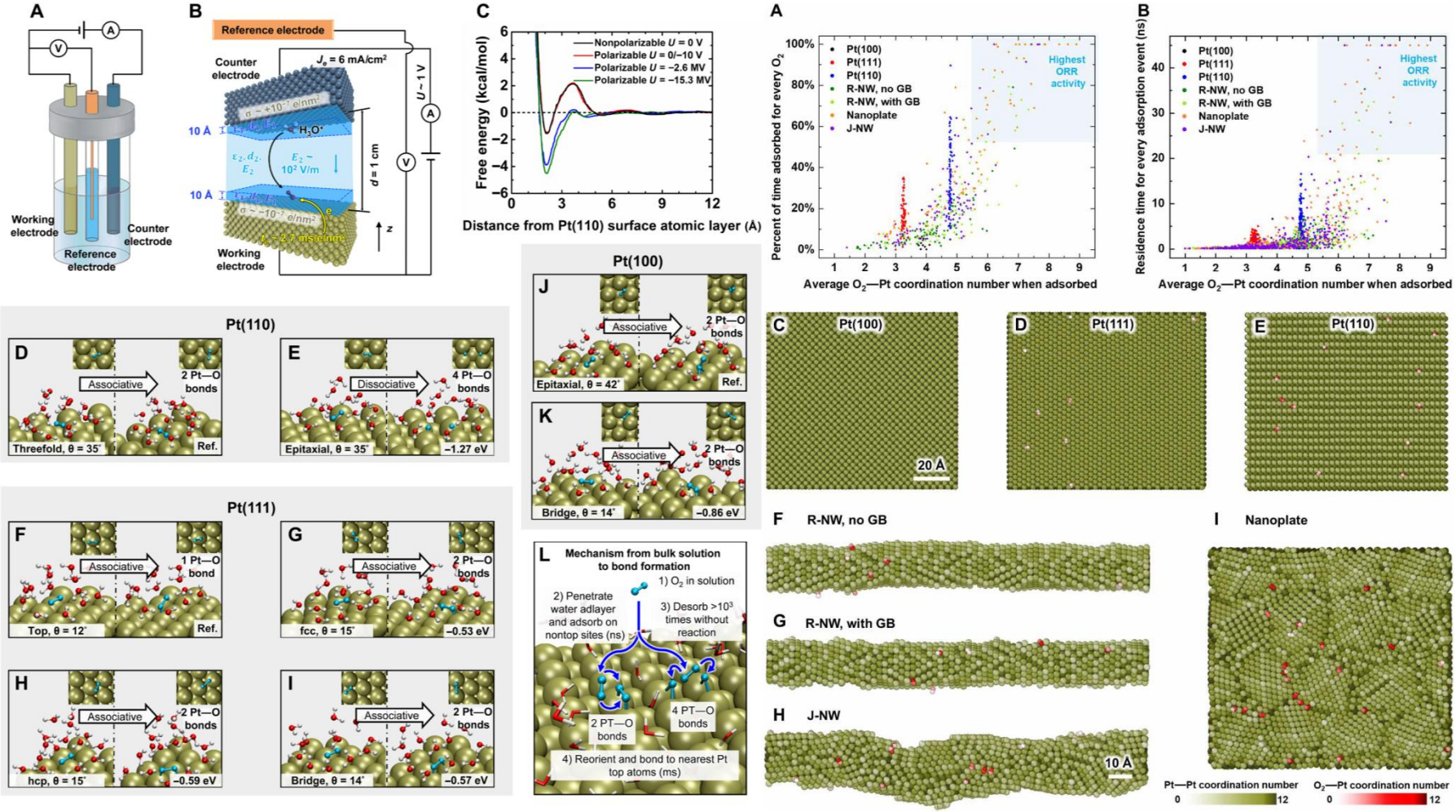


Adsorpcija na oksidima – nema jedinstvene teorije
Primer: F_2@MgO(001)





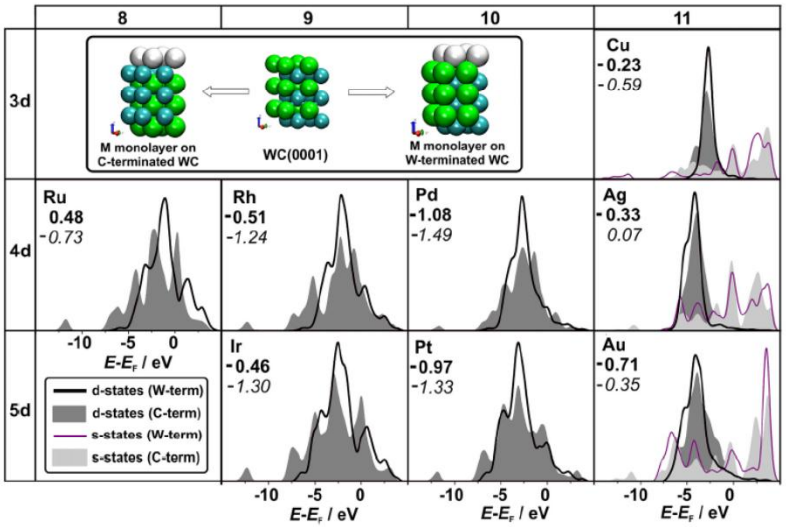
Adsorpcija i katalitička aktivnost



Wang et al., Sci. Adv. 2021; 7 : eabb1435

Adsorpcija i katalitička aktivnost

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 16071–16



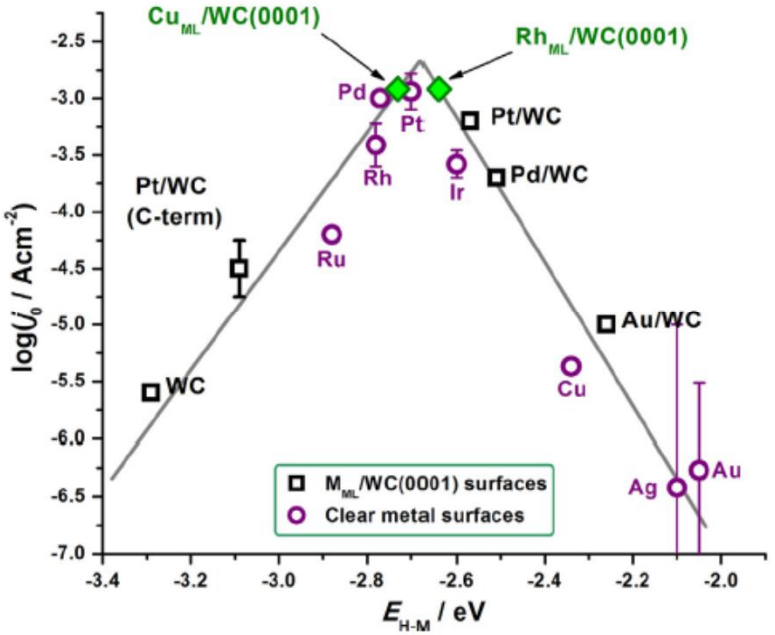


Fig. 3 – Volcano curve correlating hydrogen–metal binding energy (E_{H-M}) with corresponding experimentally determined HER activities of studied surface (expressed by log j_0, j_0 in A cm^{-2}) taken from Refs. [5,6,32,36,37], consolidating clean metal surfaces (○) and WC-based HER electrocatalysts (□). Predictions made for Cu_{ML}/WC(0001) and Rh_{ML}/WC(0001) are indicated by diamonds (◆). Error bars indicate the scattering of experimentally determined log j_0 values.