

Adsorpcija

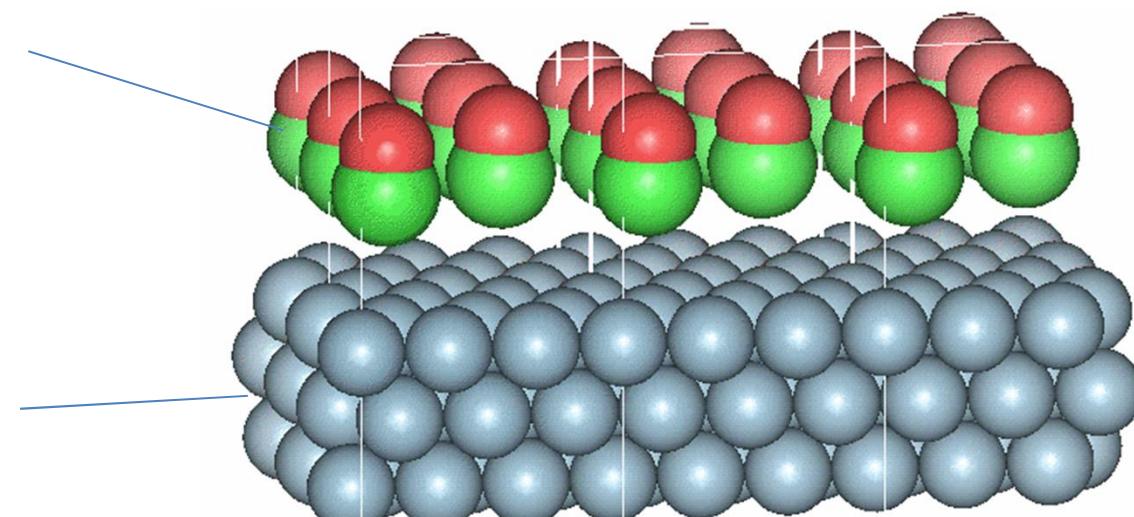
Sadržaj 1.3.

- 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

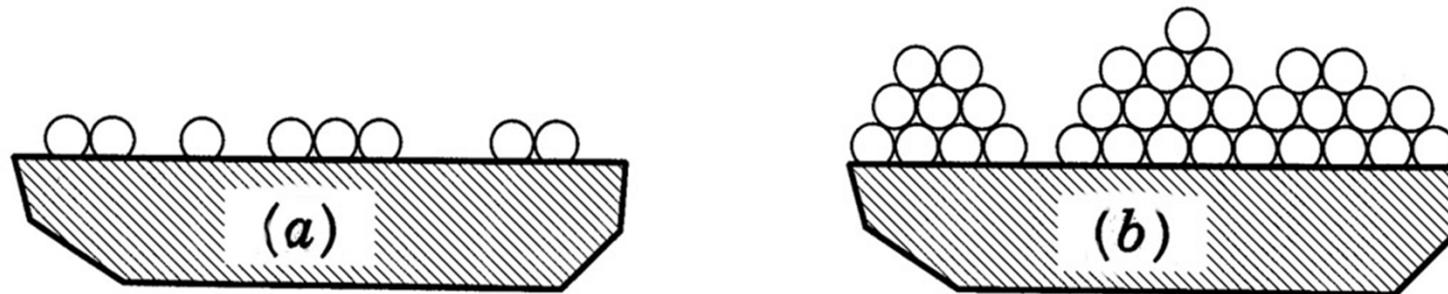
korelacija

Hemijske sile – hemisorpcija

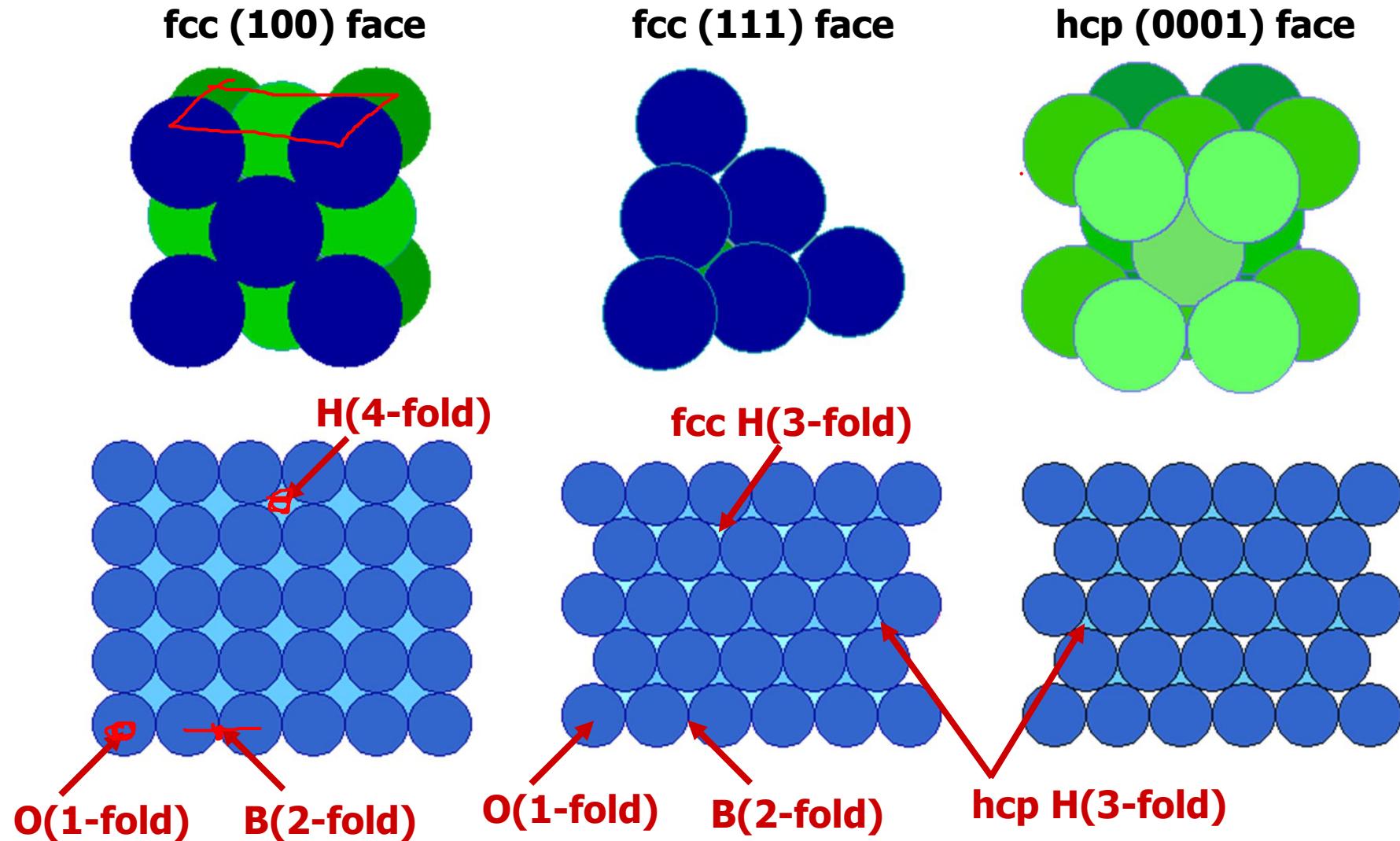
preraspodela naelektrisanja

Gustine slične tečnostima

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

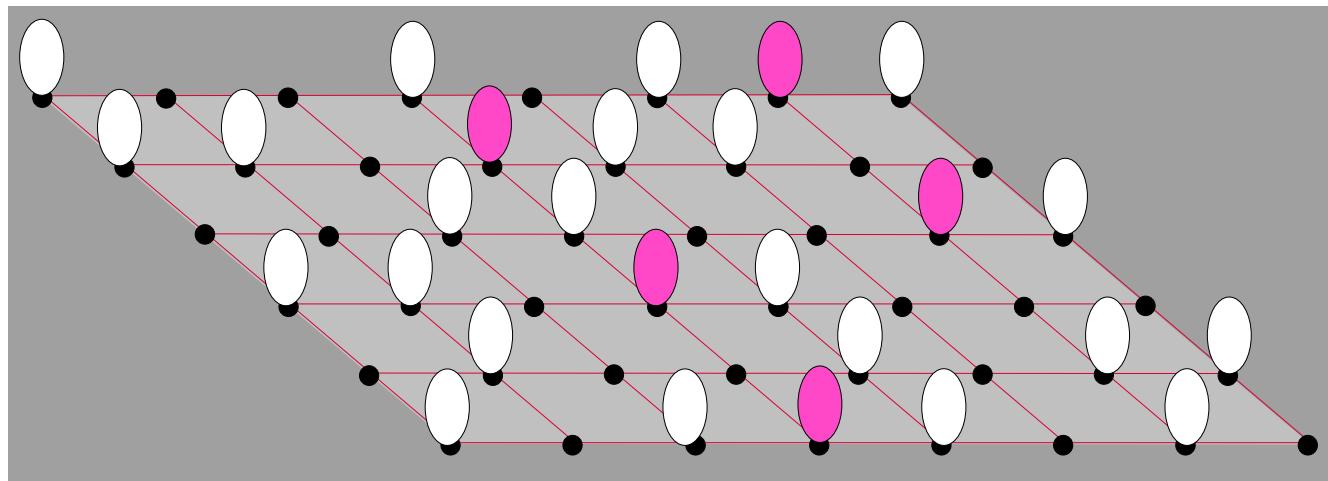


Adsorpciona mesta



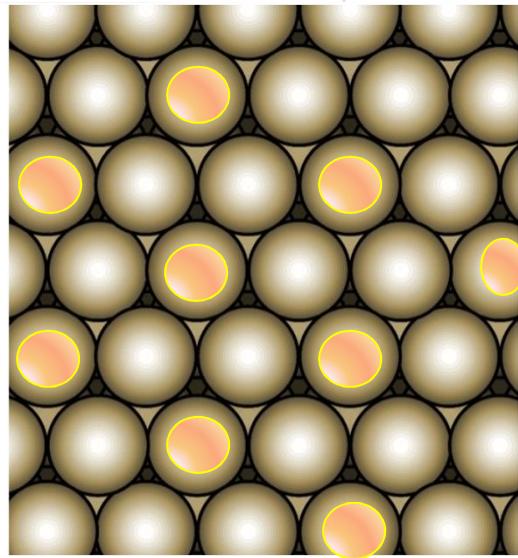
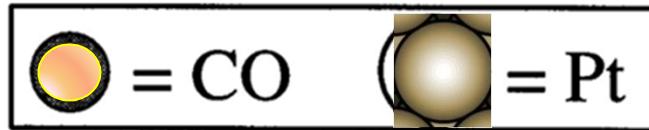
Geometrija adsorbovanih slojeva

Struktura adsorbovanih slojeva je uslovljena strukturom substrata

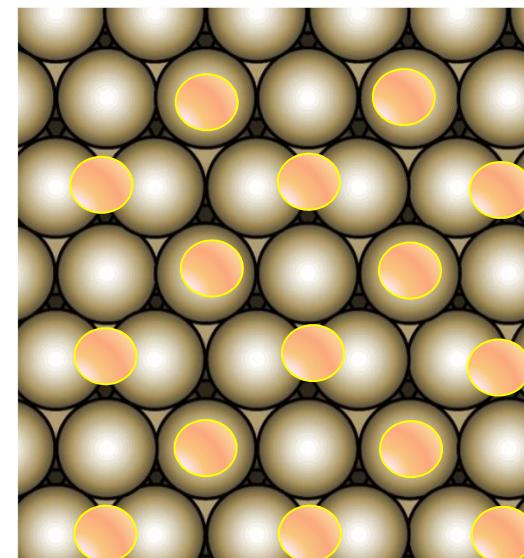


Lengmirovov tip adsorpcije na čvrstoj površini

CO na Pt(111)



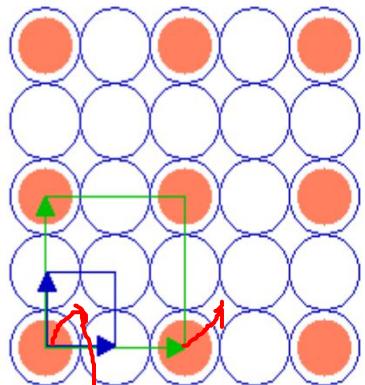
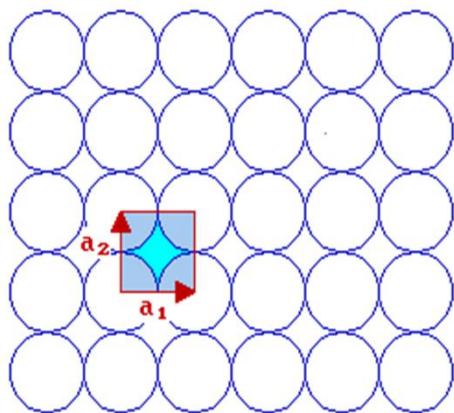
$\sqrt{3} \times \sqrt{3}$ R 30°



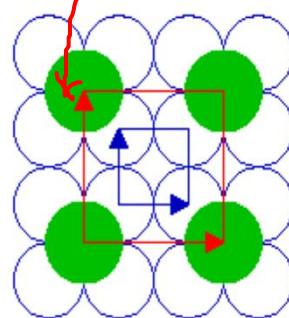
C(4x2)

Crossley & King [1980]

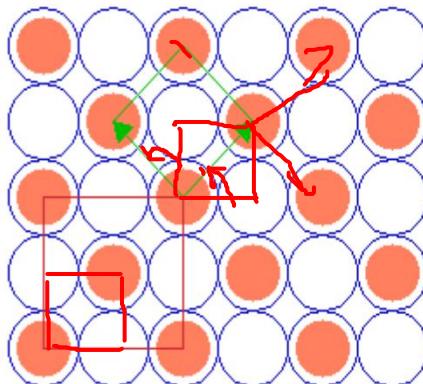
fcc (100) face



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

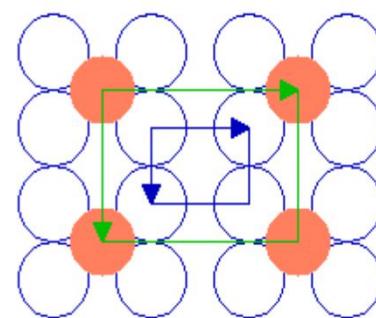
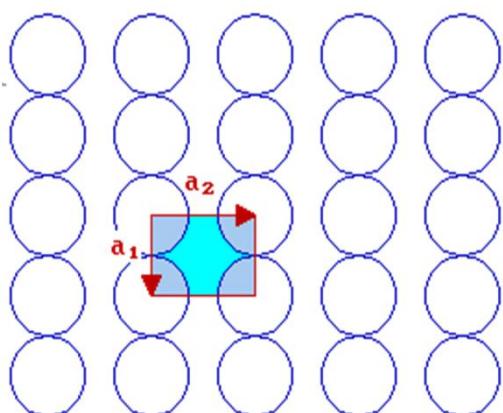


Substrate : fcc(100)
Substrate unit cell
Adsorbate unit cell

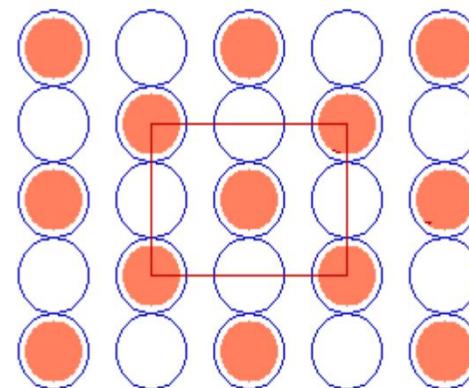


Substrate : fcc(100)
 $\text{c}(\sqrt{2} \times \sqrt{2})$
 $(\sqrt{2} \times \sqrt{2})\text{R}45$

fcc (110) face

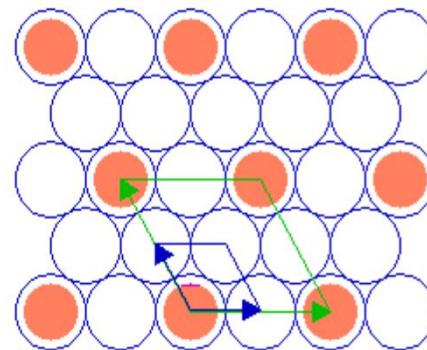
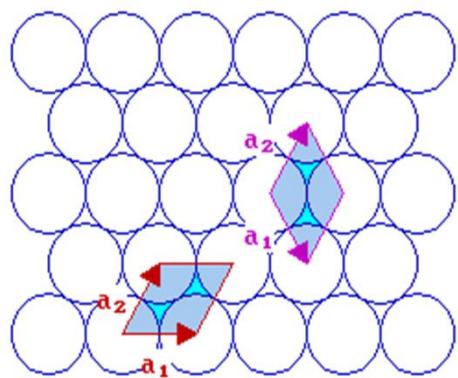


Substrate : fcc(110)
Substrate unit cell
Adsorbate unit cell

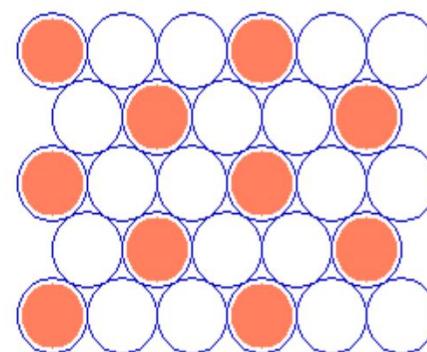


Substrate : fcc(110)
 $c(2 \times 2)$

fcc (111) face

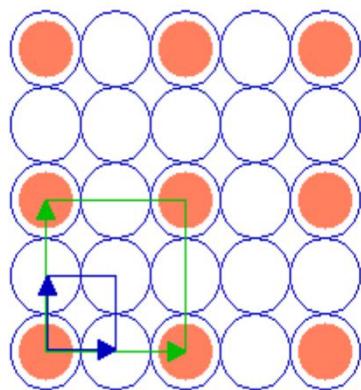


Substrate : fcc(111)
Substrate unit cell
Adsorbate unit cell



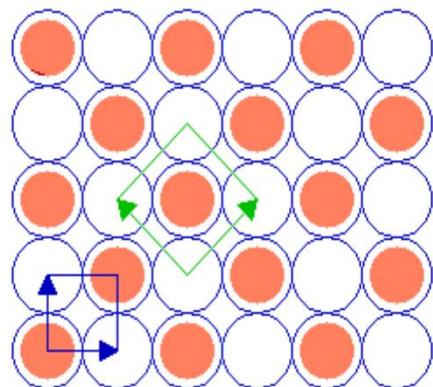
Substrate : fcc(111)
 $(\sqrt{3} \times \sqrt{3})R30$

Adsorbovani sloj: matrična notacija



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

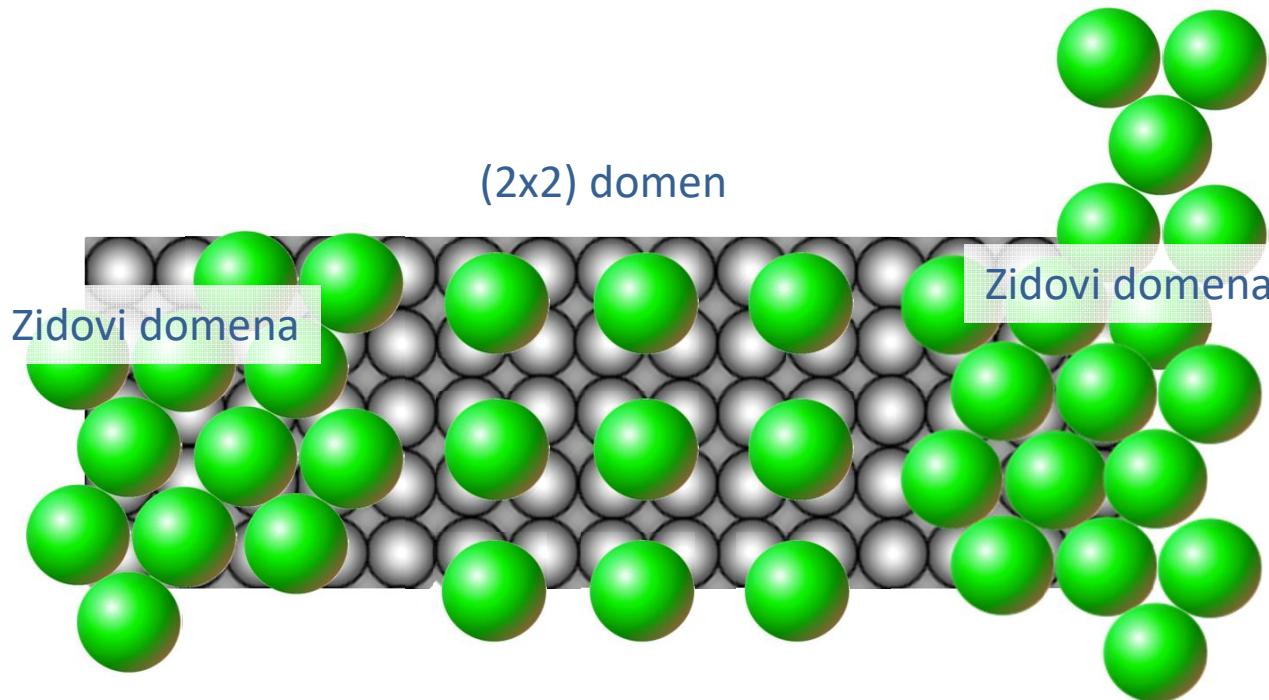
$$\begin{aligned} b_1 &= 2 \cdot a_1 + 0 \cdot a_2 \\ b_2 &= 0 \cdot a_1 + 2 \cdot a_2 \end{aligned} \Rightarrow M = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$$



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

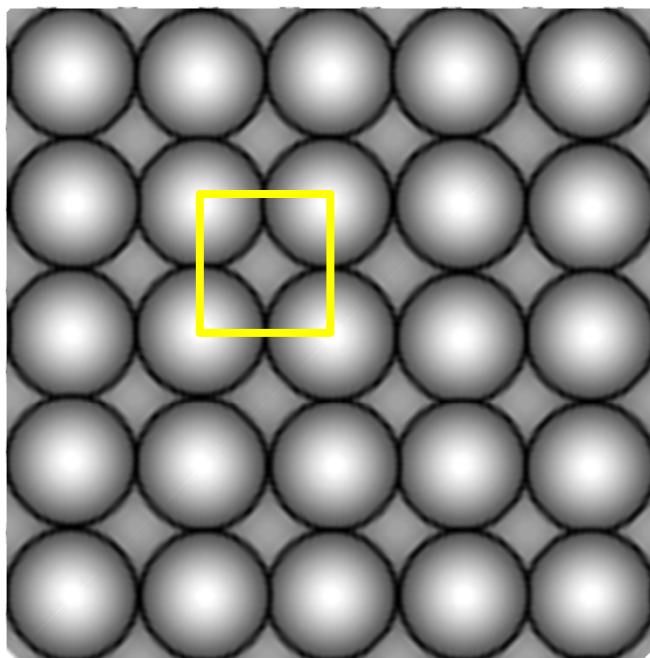
$$\begin{aligned} b_1 &= 1 \cdot a_1 + 1 \cdot a_2 \\ b_2 &= -1 \cdot a_1 + 1 \cdot a_2 \end{aligned} \Rightarrow M = \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}$$

Incommensurate Adsorption

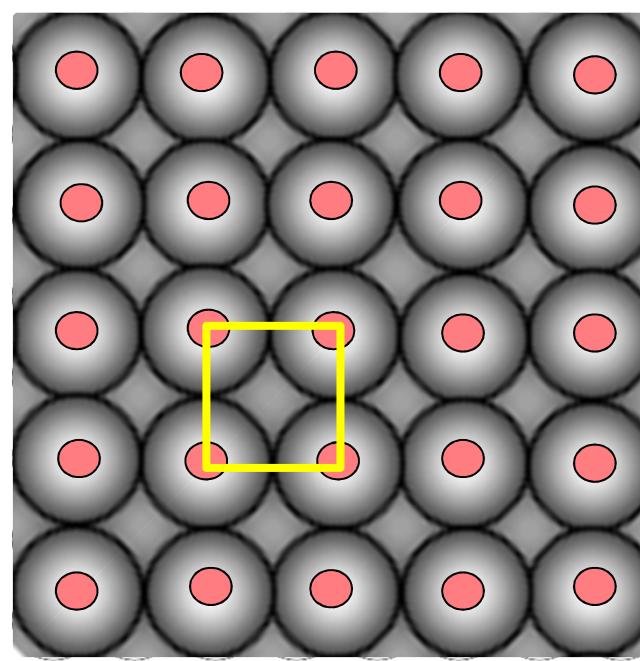


Persson et al. [1990].)

Kvadratna rešetka



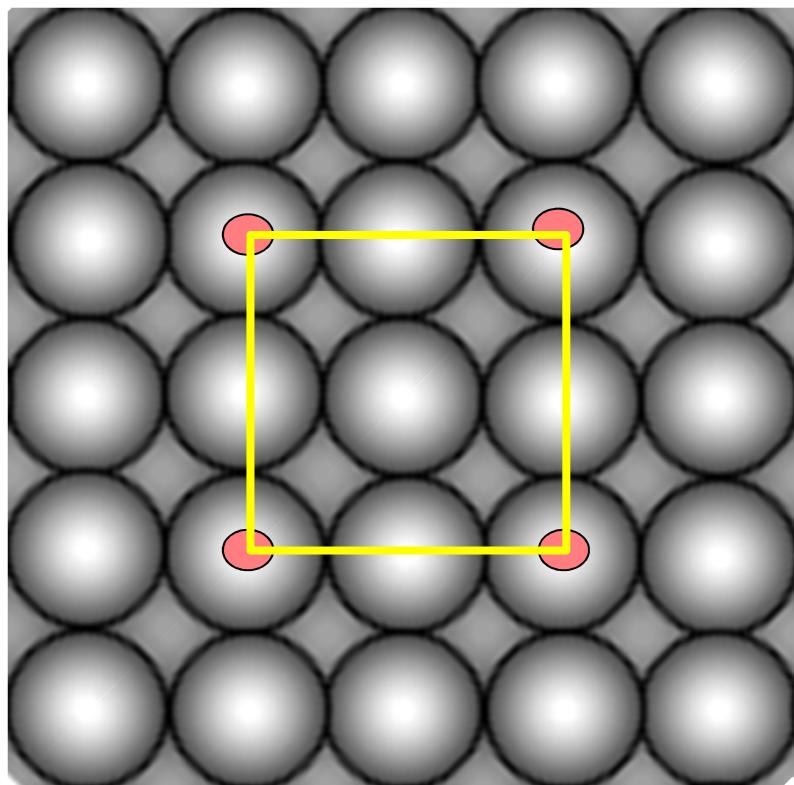
primitive unit cell



p(1x1)

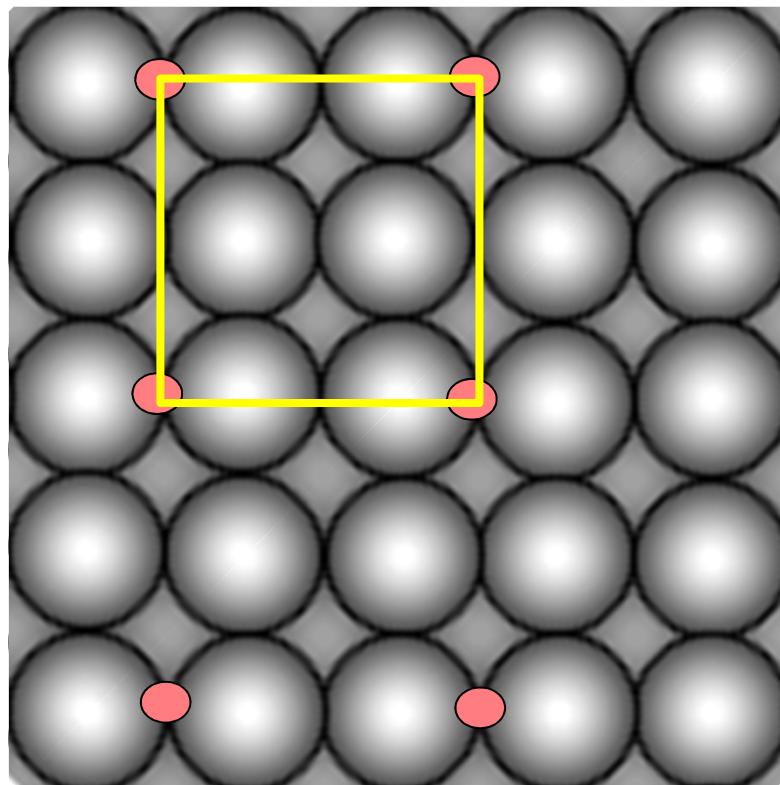
Kvadratna rešetka

c



$p(2\times 2)$

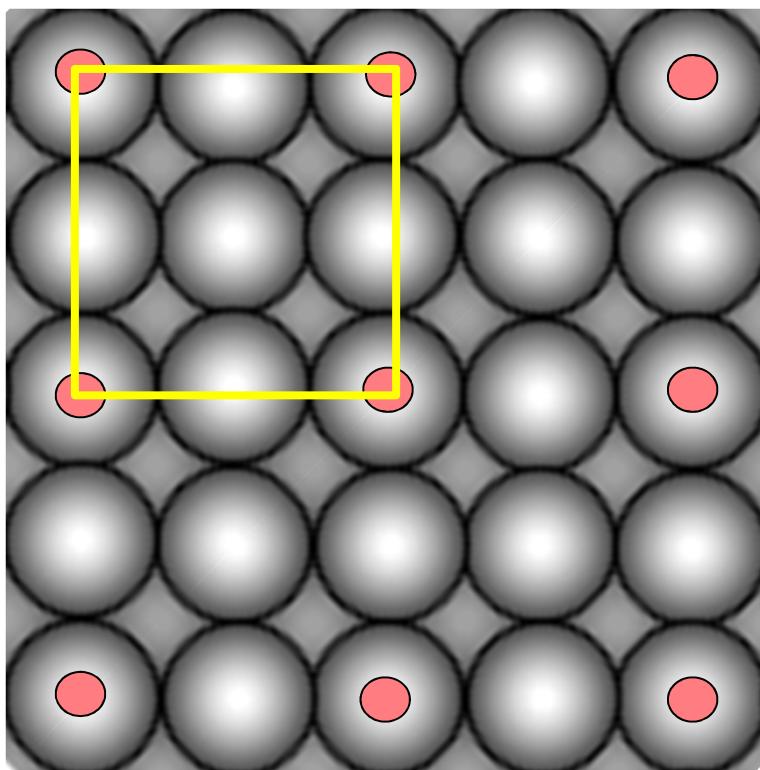
d



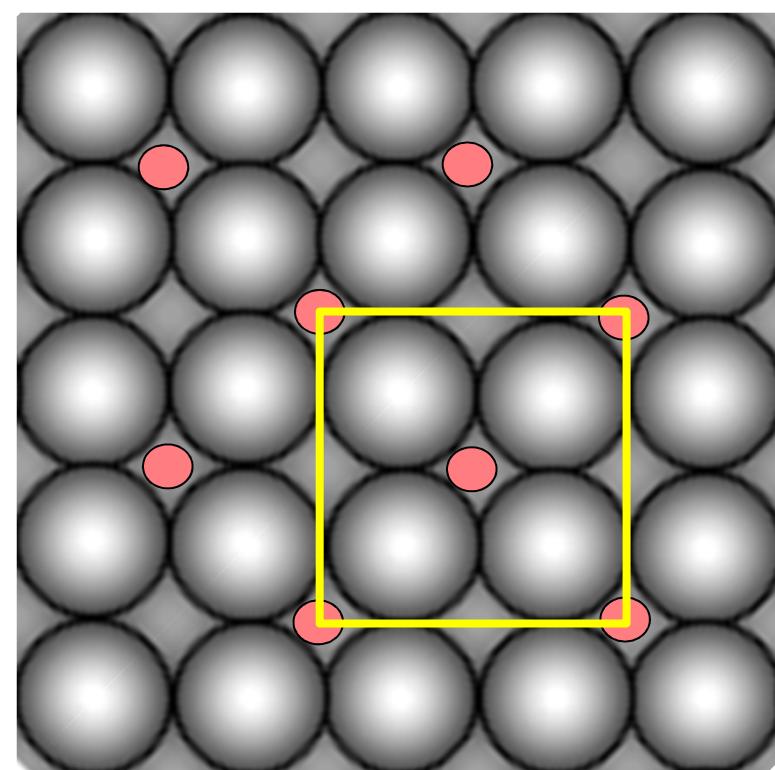
$p(2\times 2)$

Primitivna i centrirana rešetka

C

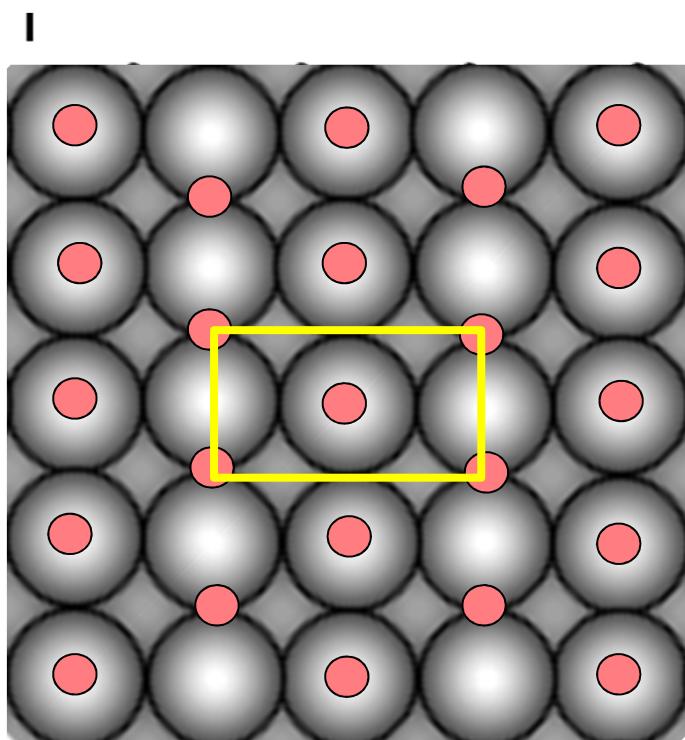


p(2x2)

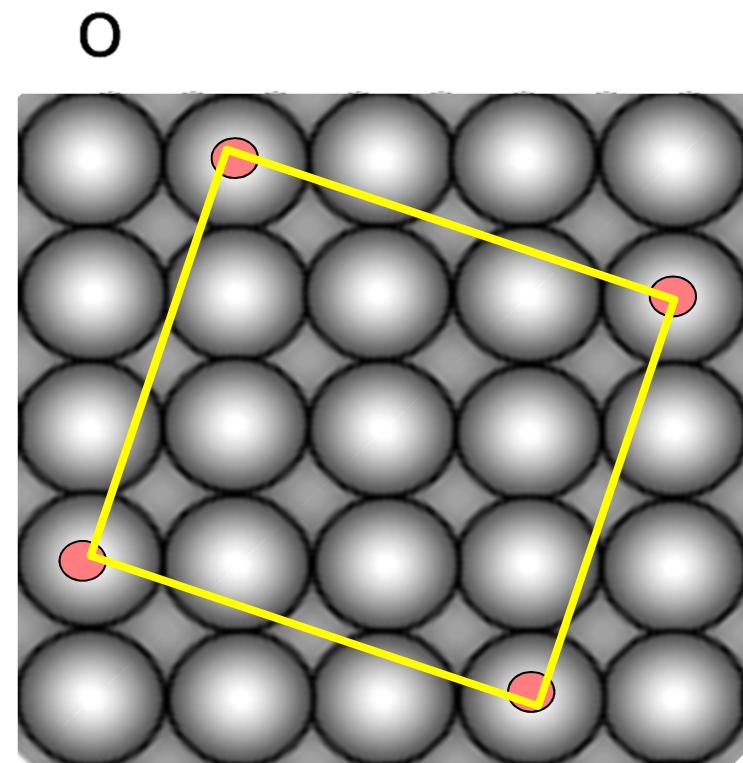


c(2x2)

Kvadratna rešetka



$\text{P}(2\times 1)$



$\sqrt{10} \times \sqrt{10} R18.4^\circ$

$\text{CH}_3\text{S}/\text{Au}(111)$

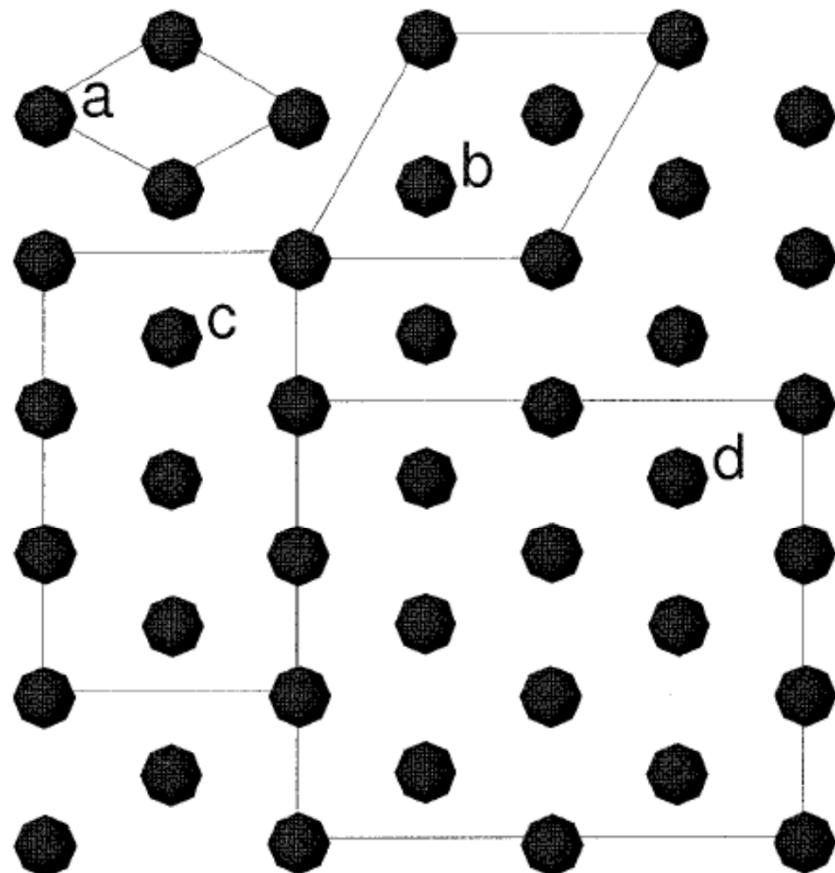
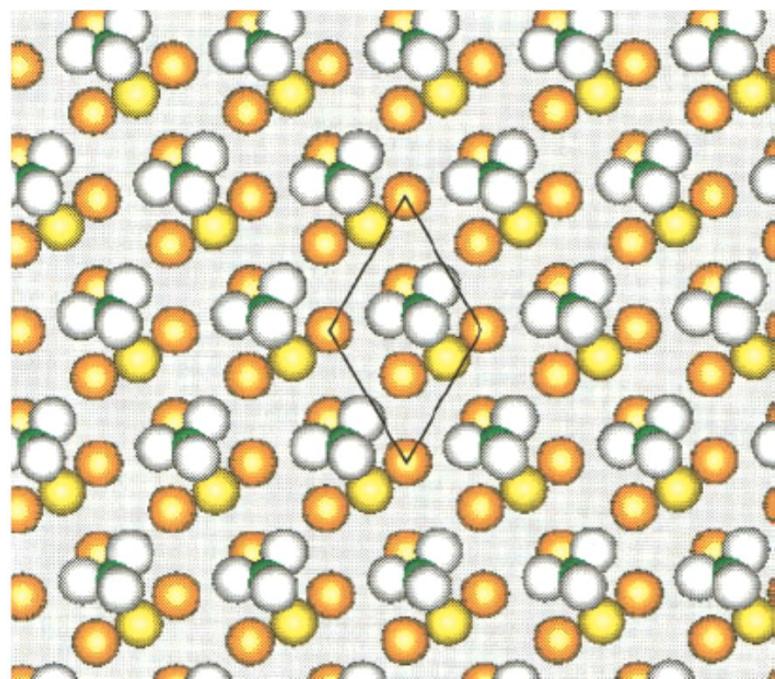
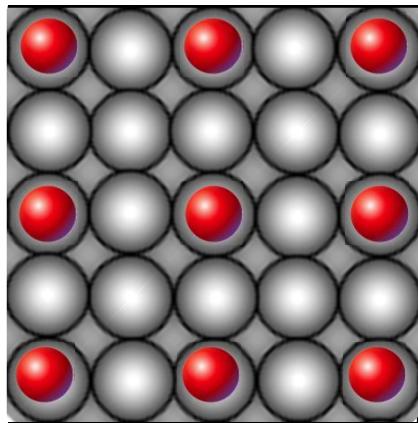


Figure 1. Surface cells used in the calculations. (a) (1×1) ; (b) $(\sqrt{3} \times \sqrt{3})\text{R}30$; (c) $(3 \times \sqrt{3})$; (d) $(3 \times 2\sqrt{3})$. These cells contain 1, 3, 6, and 12 Au atoms per layer, respectively. Cell d corresponds to the $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})\text{R}30$ lattice.

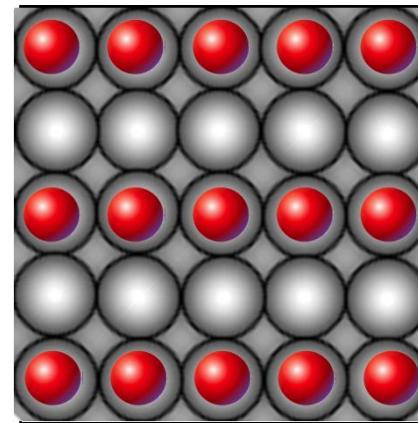
Θ	site	Δz	S-M	E_{ads}	cell
1	~on-top	2.84	3.00	4.4	c
1	~on-top	2.86	3.00	5.8	d
0.5	~on-top	2.84	2.98	5.9	d
1	fcc hollow	1.81	2.59	2.9	b
0.5	fcc hollow	1.60	2.51	11.5	c
0.25	fcc hollow	1.59	2.51	18.3	d
1	hcp hollow	1.90	2.60	-1.1	b
0.5	hcp hollow	1.70	2.53	4.7	c
1	bridge	2.09	2.52	18.6	b
0.5	bridge	2.07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



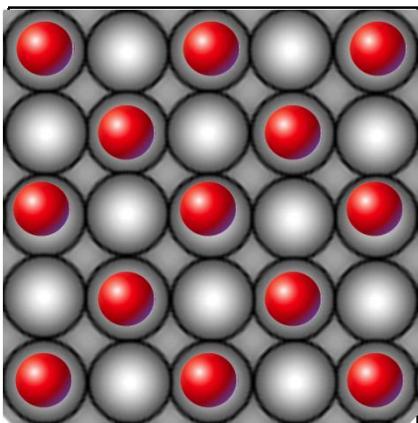
Adsorpcija CO na kvadratnoj rešetki – adsorbovane faze



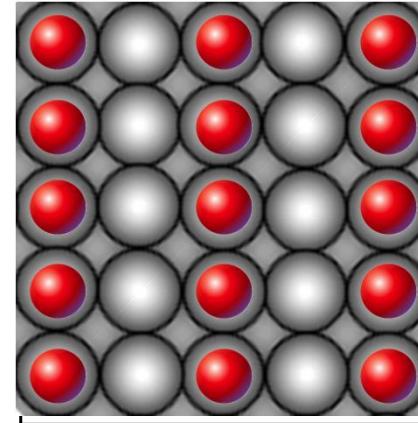
P(2x2)



(2x1)



C(2x2)



(1x2)

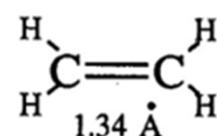
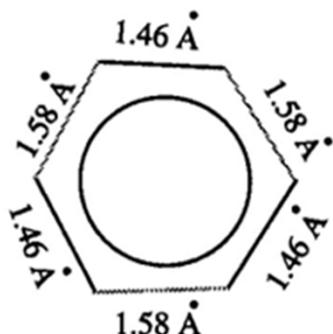
The absorption of molecules in a p(2x2), C(2x2), (2x1) overlayer. The dark circles represent sites, the red circles represent adsorption on the sites.

Hemisorpcija na metalima

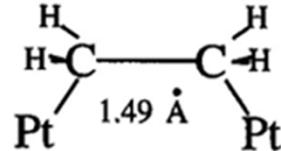
- Metali imaju mnogo slobodnih elektrona koji učestvuju u vezivanju
- Veza je delokalizovana
- Elektroni su pokretni

Adsorpcija je kompromis – da bude dobro i adsorbatu i substratu

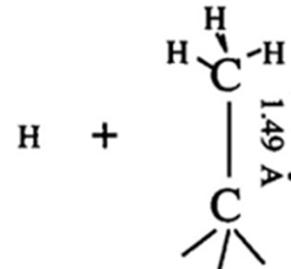
Mehanizam aktivacije hemijske veze u katalizi



Gaseous Ethylene



Ethylene On 100 K Pt(111)



Ethylene On 300 K Pt(111)



Gaseous Hydrogen



Hydrogen On Platinum

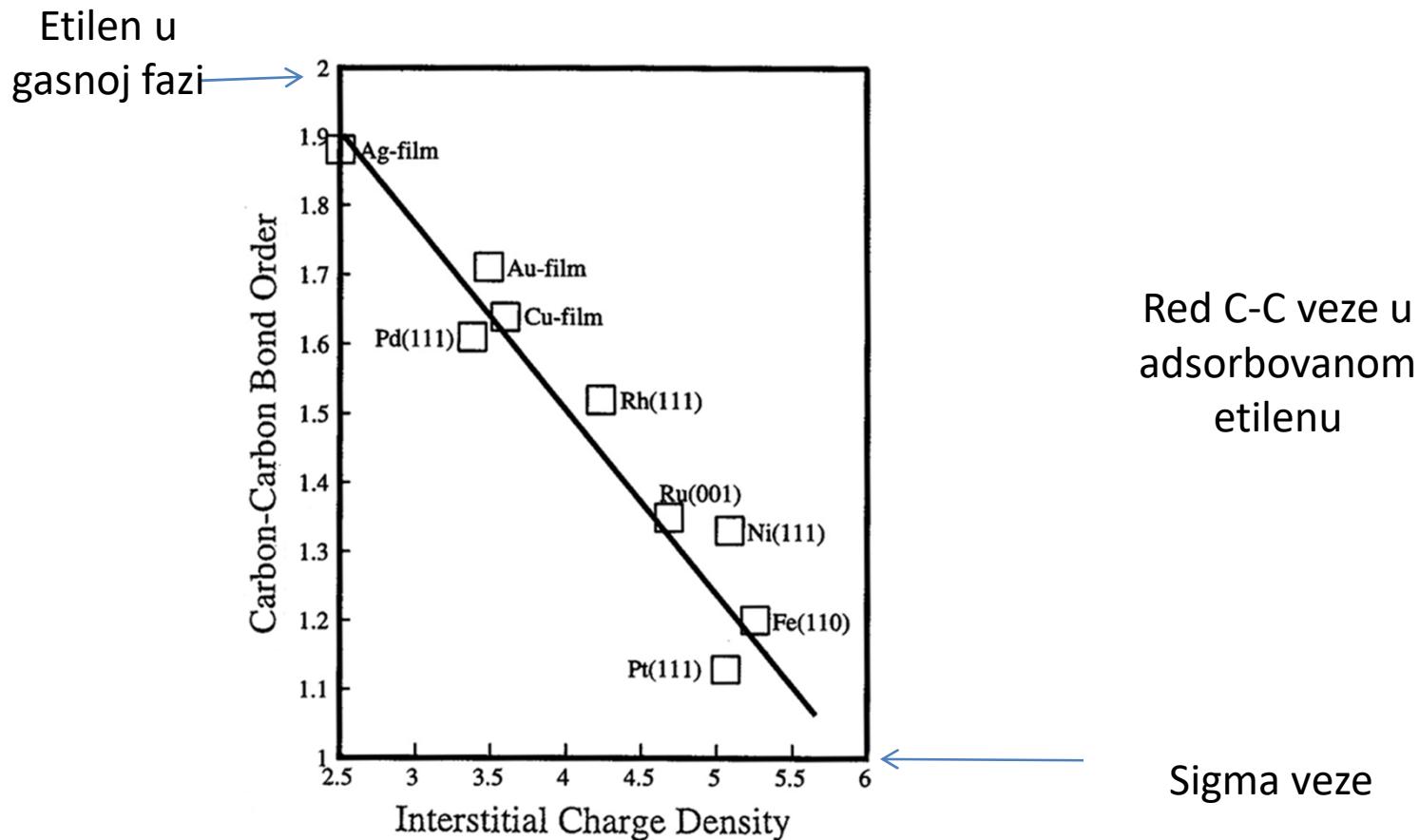
Trendovi u periodnom sistemu

Periodic Table of the Elements

The table includes element symbols and atomic numbers. The first two rows show H (1) and He (2). The third row shows Li (3), Be (4), Na (11), and Mg (12). The fourth row shows K (19), Ca (20), Sc (21), Ti (22), V (23), Cr (24), Mn (25), Fe (26), Co (27), Ni (28), Cu (29), Zn (30), Ga (31), Ge (32), As (33), Se (34), Br (35), and Kr (36). The fifth row shows Rb (37), Sr (38), Y (39), Zr (40), Nb (41), Mo (42), Tc (43), Ru (44), Rh (45), Pd (46), Ag (47), Cd (48), In (49), Sn (50), Sb (51), Te (52), I (53), and Xe (54). The sixth row shows Cs (55), Ba (56), La (57), Hf (72), Ta (73), W (74), Re (75), Os (76), Ir (77), Pt (78), Au (79), Hg (80), Ti (81), Pb (82), Bi (83), Po (84), At (85), and Rn (86). The seventh row shows Fr (87), Ra (88), Ac (89), Unq (104), Unp (105), Unh (106), Uns (107), Uno (108), Une (109), and Unn (110). The bottom section shows the lanthanide series from Ce (58) to Lu (71), followed by Th (90), Pa (91), U (92), Np (93), Pu (94), Am (95), Cm (96), Bk (97), Cf (98), Es (99), Fm (100), Md (101), No (102), and Lr (103).

H ¹																He ²	
Li ³	Be ⁴															Ne ¹⁰	
Na ¹¹	Mg ¹²															Ar ¹⁸	
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰	Ti ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Unq ¹⁰⁴	Unp ¹⁰⁵	Unh ¹⁰⁶	Uns ¹⁰⁷	Uno ¹⁰⁸	Une ¹⁰⁹	Unn ¹¹⁰								
Ce ⁵⁸	Pr ⁵⁹	Nd ⁶⁰	Pm ⁶¹	Sm ⁶²	Eu ⁶³	Gd ⁶⁴	Tb ⁶⁵	Dy ⁶⁶	Ho ⁶⁷	Er ⁶⁸	Tm ⁶⁹	Yb ⁷⁰	Lu ⁷¹				
Th ⁹⁰	Pa ⁹¹	U ⁹²	Np ⁹³	Pu ⁹⁴	Am ⁹⁵	Cm ⁹⁶	Bk ⁹⁷	Cf ⁹⁸	Es ⁹⁹	Fm ¹⁰⁰	Md ¹⁰¹	No ¹⁰²	Lr ¹⁰³				

Često dobra korelacija između elektronske gustine, elektronegativnosti i adsorpcionih svojstava



Adsorpcija kroz periodni sistem

H														
Li	Be													
Na	Mg													
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	
a	b	c	d	e										

Klasifikacija prema reaktivnosti površine

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

Kvalitativni aspekti

Metal	Adsorbing Gas			
	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

The periodic table shows the following regions highlighted:

- Group a:** Hydrogen (H) and Helium (He).
- Group b:** Lithium (Li), Beryllium (Be), Sodium (Na), Magnesium (Mg), Potassium (K), Calcium (Ca), Scandium (Sc), Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Gallium (Ga), Germanium (Ge), Rubidium (Rb), Strontium (Sr), Yttrium (Y), Zirconium (Zr), Niobium (Nb), Molybdenum (Mo), Technetium (Tc), Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Silver (Ag), Cadmium (Cd), Indium (In), Tin (Sn), Cesium (Cs), Barium (Ba), Lanthanum (La), Hafnium (Hf), Tantalum (Ta), Tungsten (W), Rhenium (Re), Osmium (Os), Iridium (Ir), Platinum (Pt), Gold (Au), Mercury (Hg), Thallium (Tl), Lead (Pb).
- Group c:** A column below group b.
- Group d:** A column below group c.
- Group e:** A column below group d.

0 – nema adsorpcije

1 – ima na 100 K ali nema na 300 K

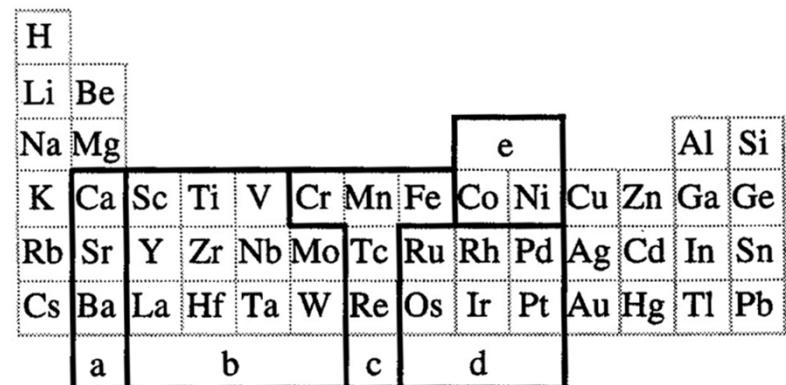
2 – aktivirani proces

3 – brza adsorpcija na sobnoj temperaturi

Nedovoljna elektronska
gustina

Kvalitativni aspekti

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 ₂ O 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	CH_4	CH_3OH	H_2O
	C_2H_4	C_2H_6		
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

The periodic table shows the following highlights:

- Group a:** Elements H, Be, Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, and Pb are grouped together.
- Group b:** Elements Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, and Hg are grouped together.
- Group c:** Elements La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, and Pb are grouped together.
- Group d:** Elements a, b, c, d, and e are highlighted in boxes below the main body of the table.
- Group e:** Elements Al and Si are highlighted in the top right corner.

0 – nema adsorpcije

1 – ima na 100 K ali nema na 300 K

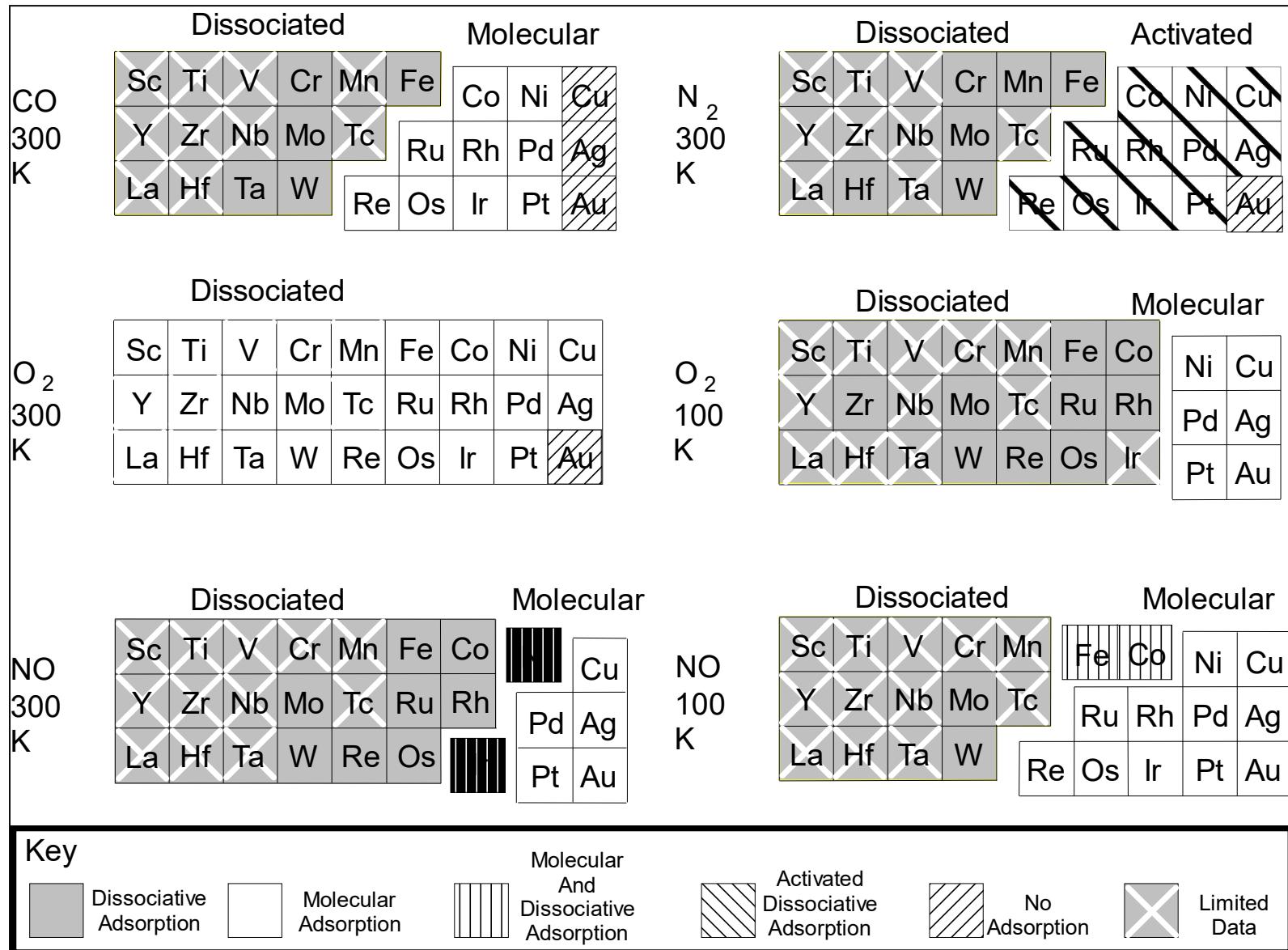
2 – aktivirani proces

3 – brza adsorpcija na sobnoj temperaturi

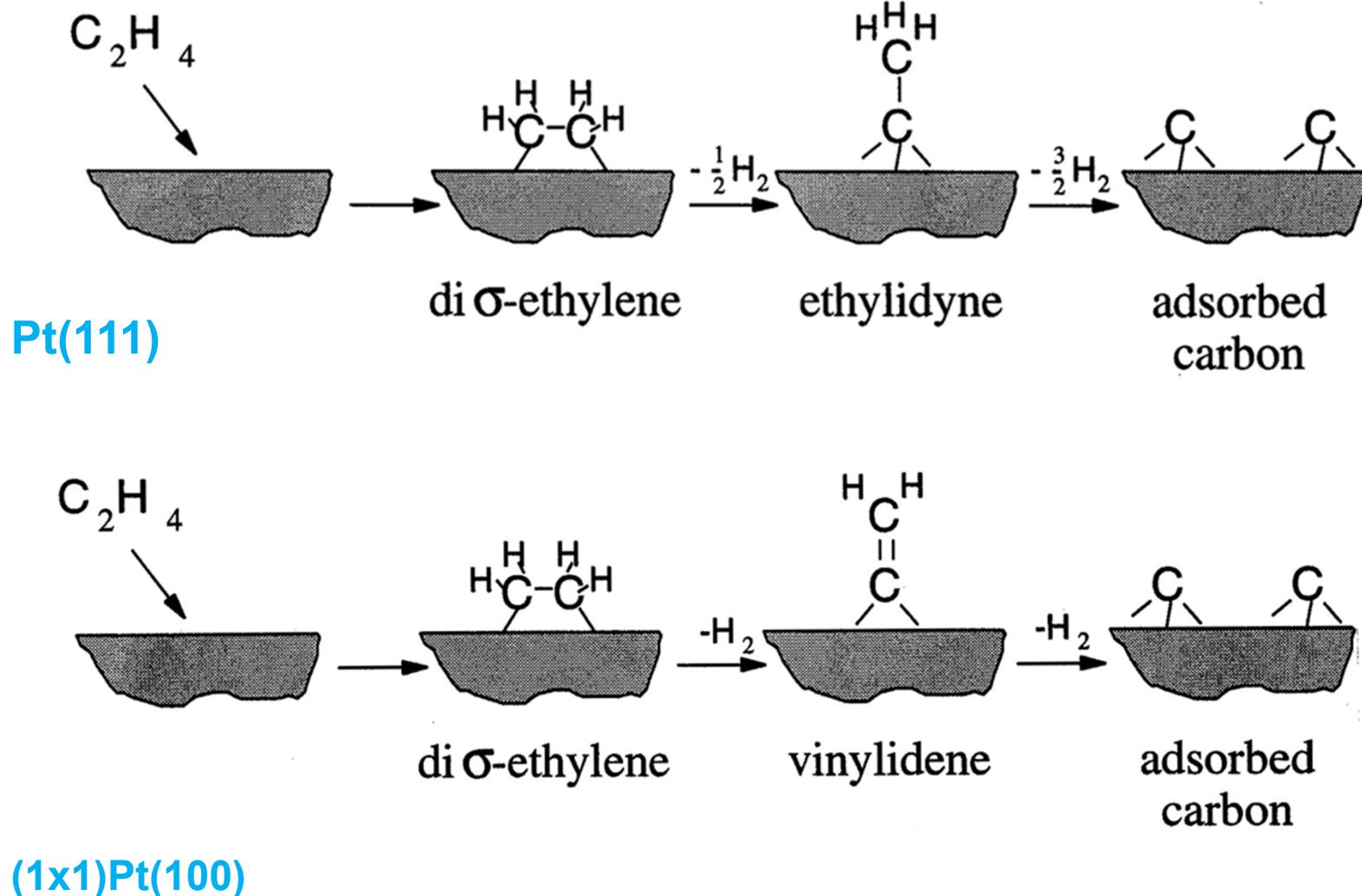
Molekulska i disocijativna adsorpcija

Brodén et al. [1976]

10^{-6} torr



Strukturna osetljivost



Različite klase adsorbata na metalnim površinama

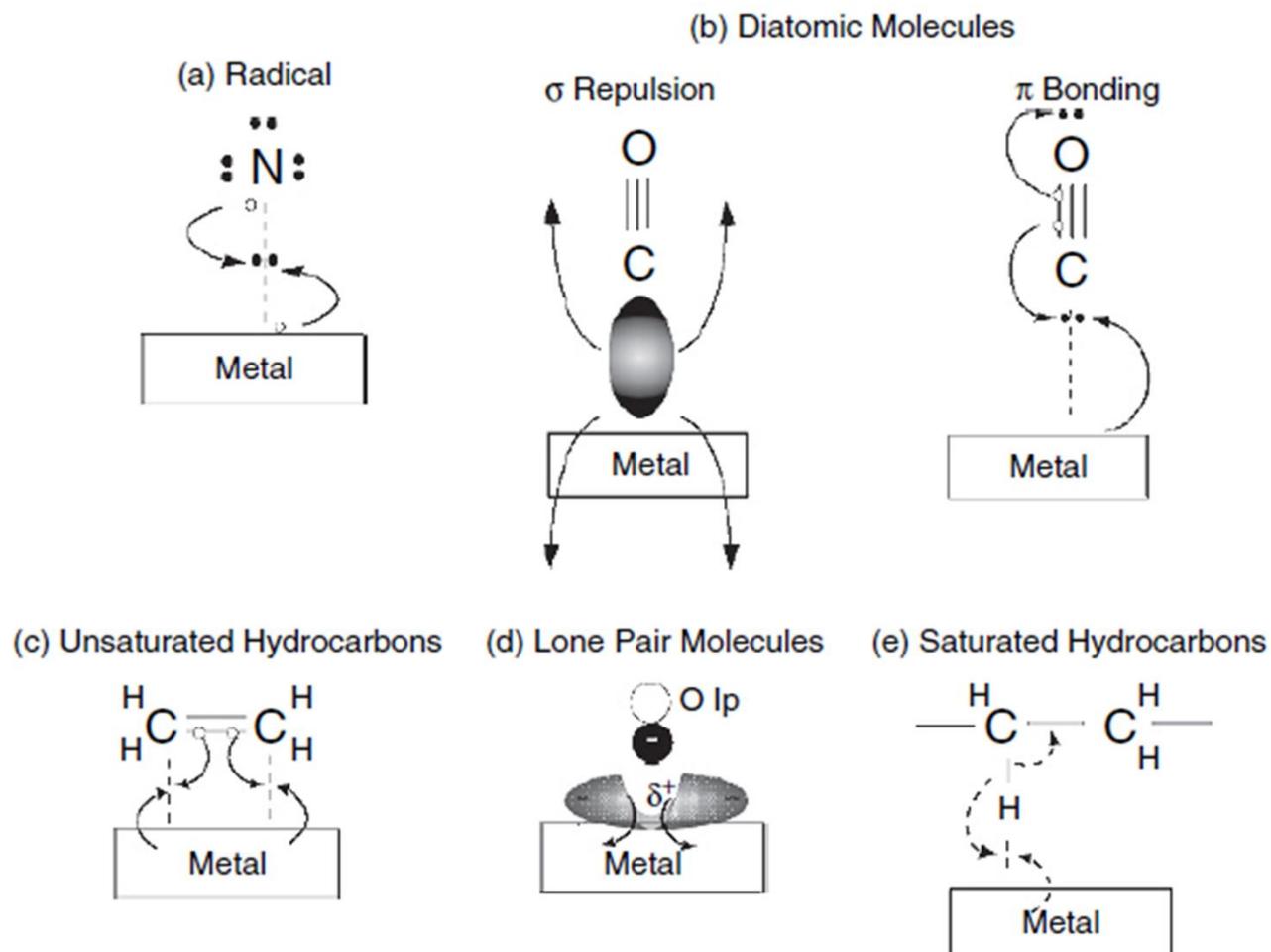
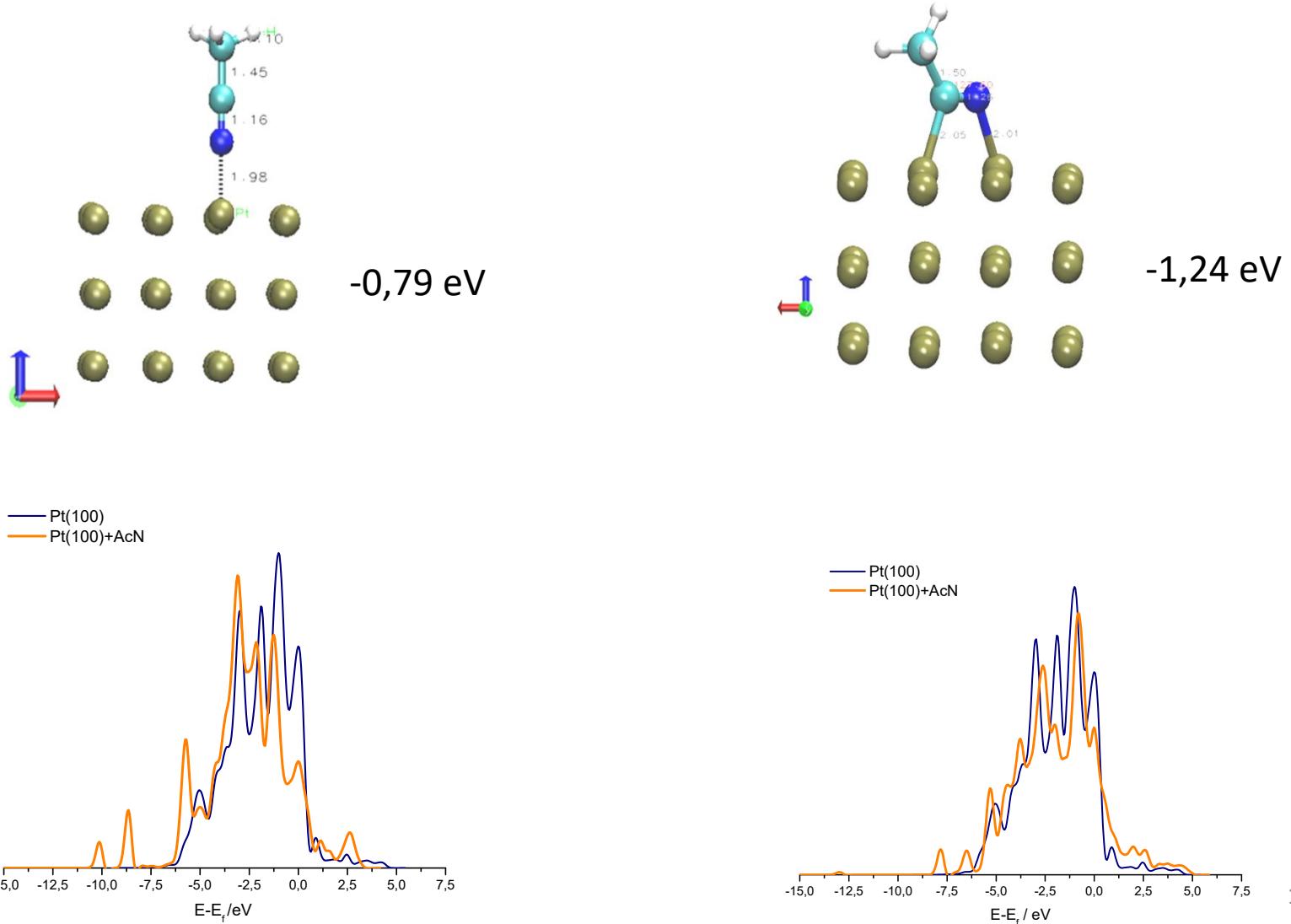


Figure 2.58. Schematic illustrations of the five different types of chemical bond formation on metal surfaces. 110

Primer: AcN na Pt(001)



Korelacija sa elektronskom strukturom

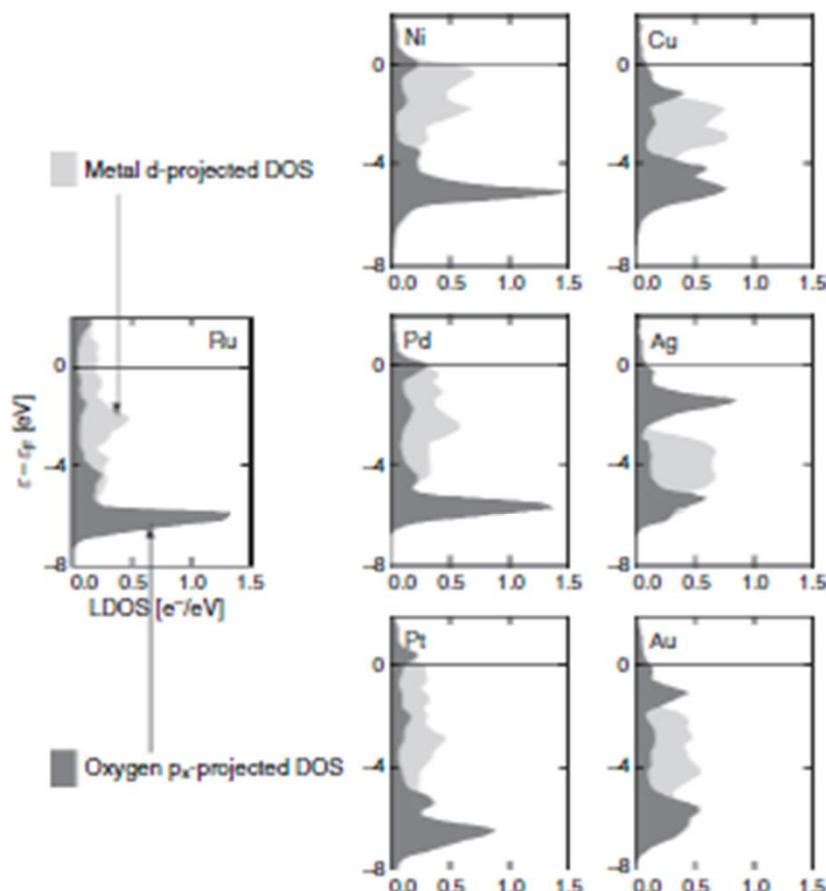


Figure 4.2. The density of states projected onto the d states of the surface atoms for the surfaces considered in Figure 4.1 (grey). Also shown (black) is the oxygen 2p_x projected density of states for O adsorbed on the same surfaces. The formation of bonding and anti-bonding states below and above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

Korelacija sa elektronском структуром

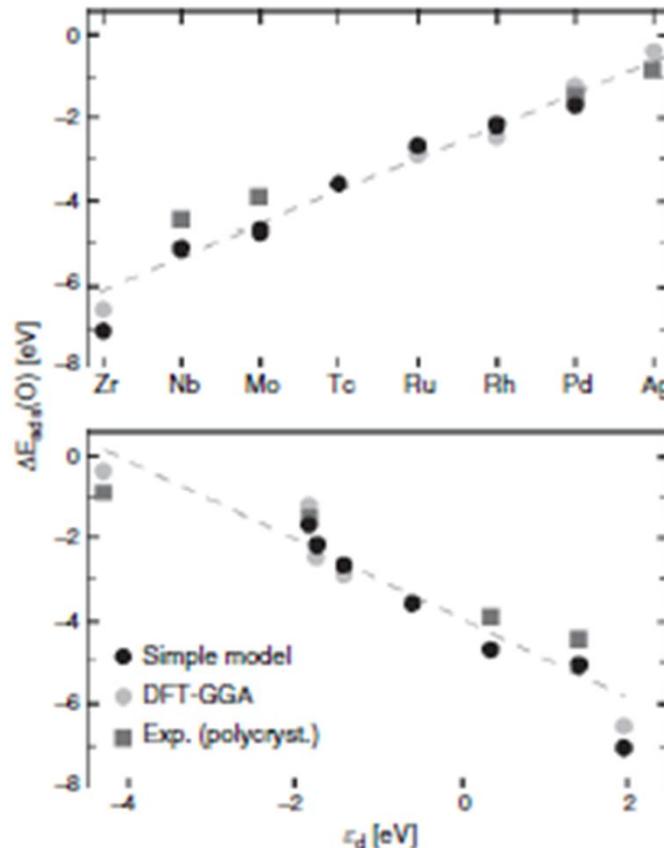
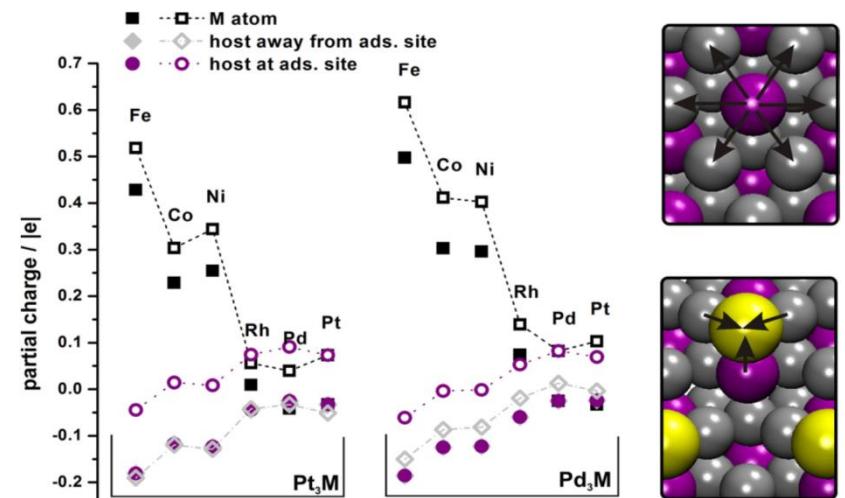
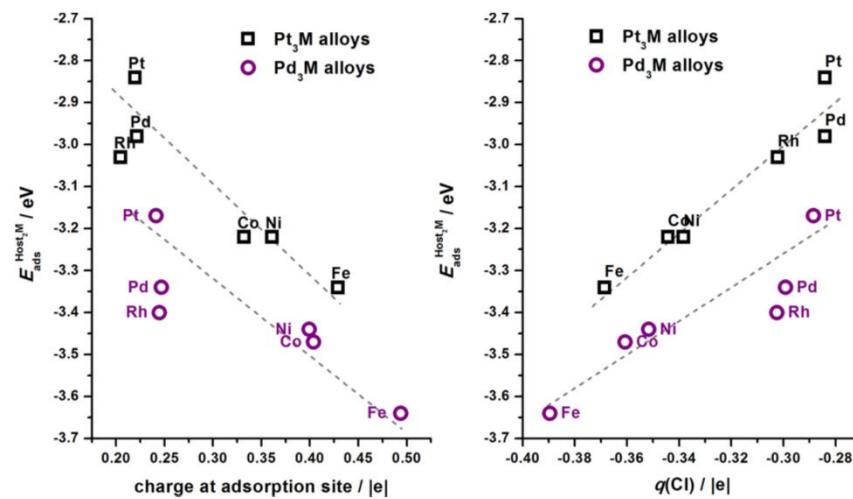
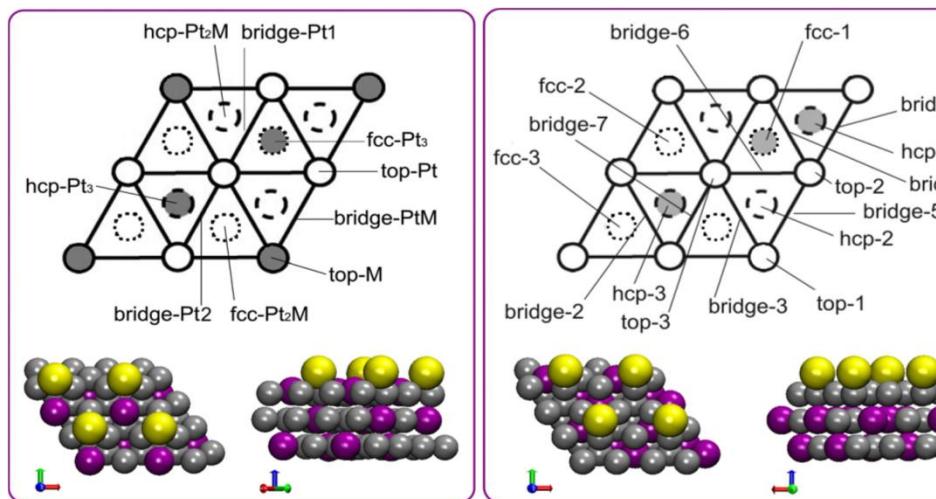


Figure 4.6. Variations in the O adsorption energy along the 4d transition metal series. The results of full DFT calculations are compared to those from the simple d band model and to experiments. Below the same data are plotted as a function of the d band center. Adapted from Ref. [4].

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

Korelacija sa elektronskom struktururom



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

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Korelacija sa elektronskom strukturom

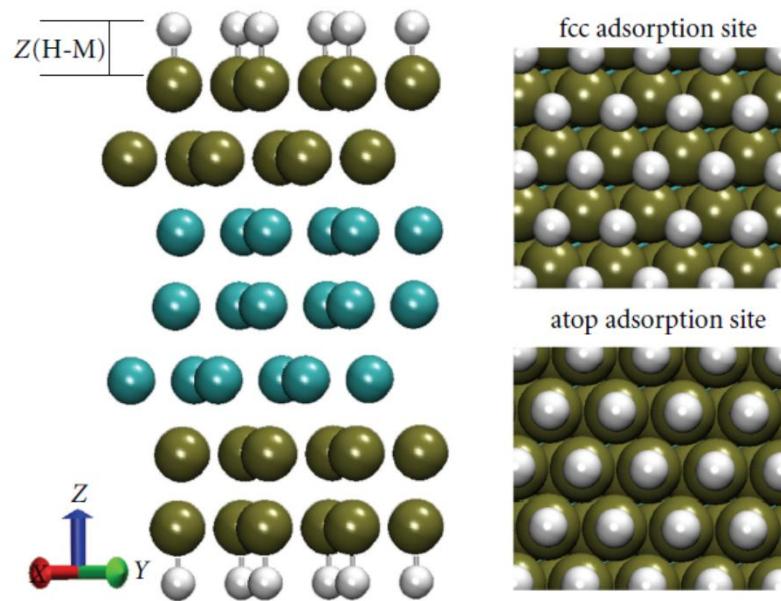


FIGURE 1: A side view of the metal slabs applied for hydrogen adsorption analysis and a perpendicular view of the surface covered with hydrogen adsorbed on fcc and atop site. For graphical representations, Visual Molecular Dynamics was used [22].

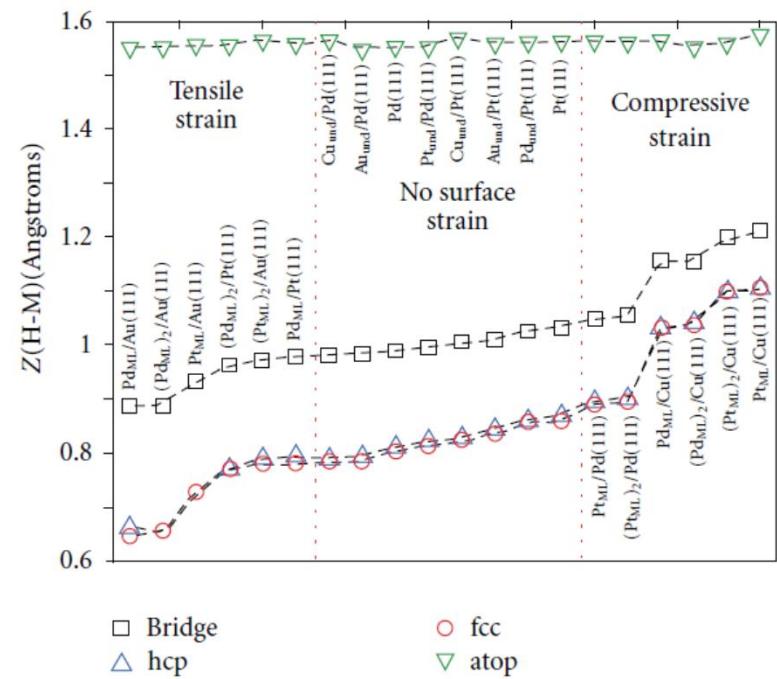
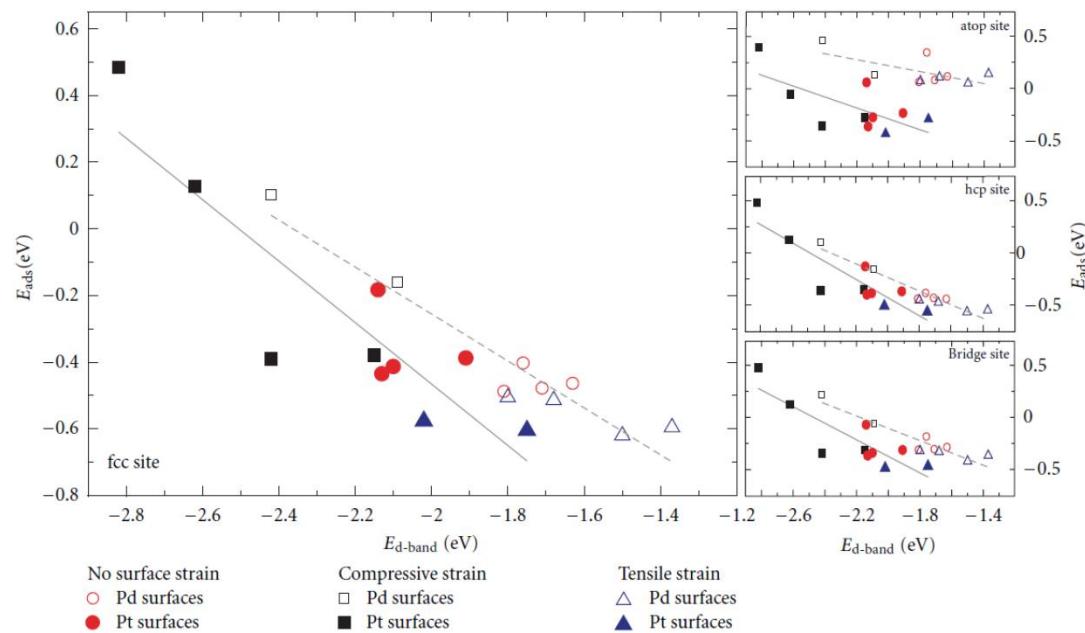


FIGURE 2: Calculated values of $Z(H-M)$ on fcc (circles), hcp (up triangles), atop (down triangles), and bridge sites (squares).

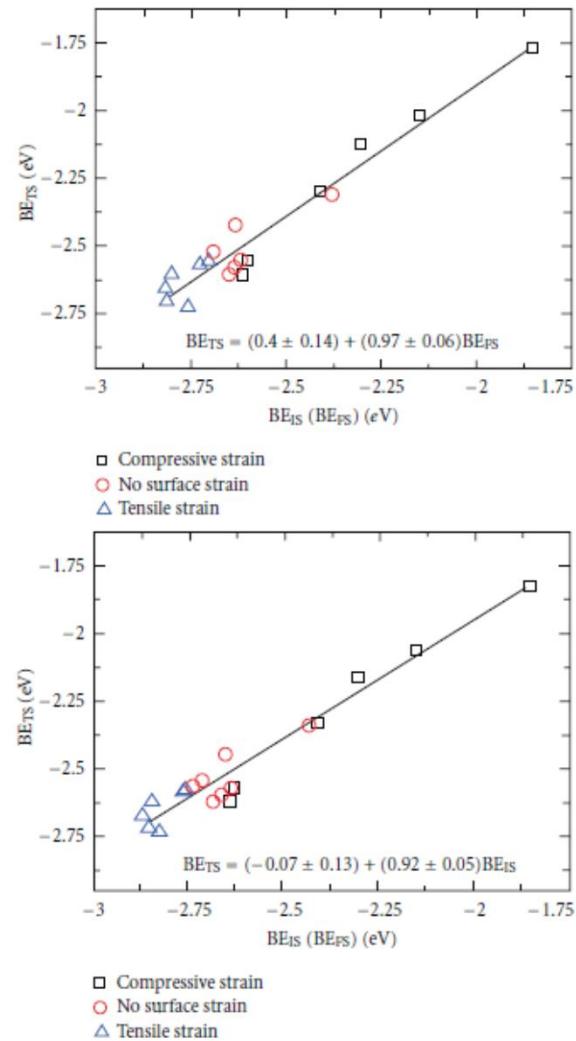
Advances in Physical Chemistry
Volume 2011, Article ID 305634, 8 pages
doi:10.1155/2011/305634

Korelacija sa elektronskom strukturom

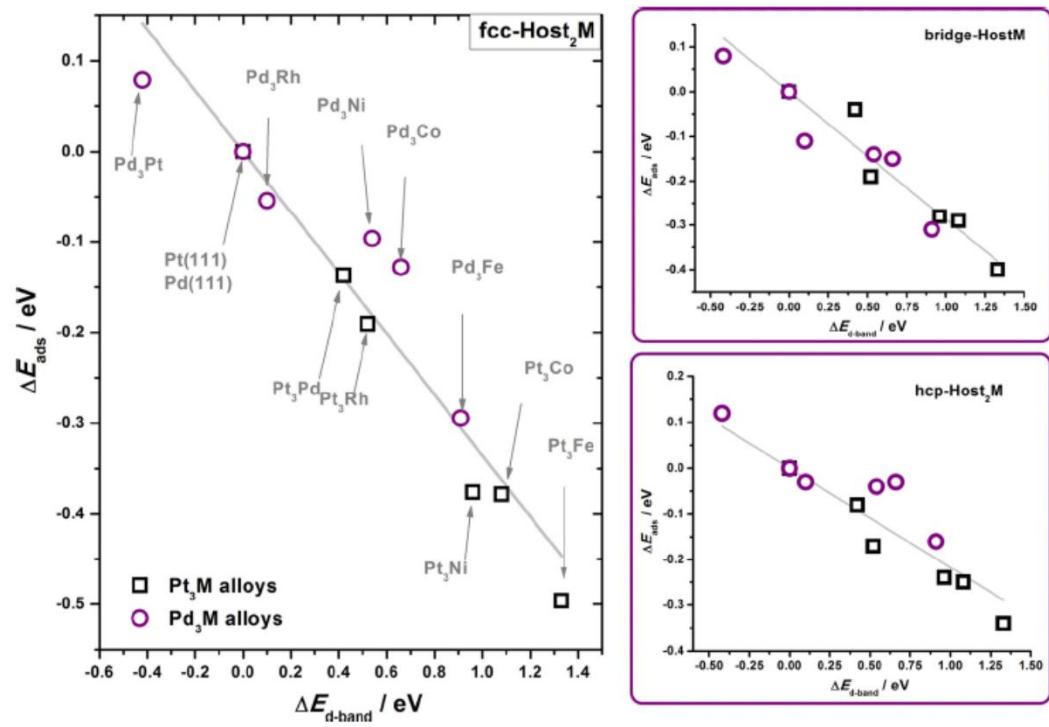
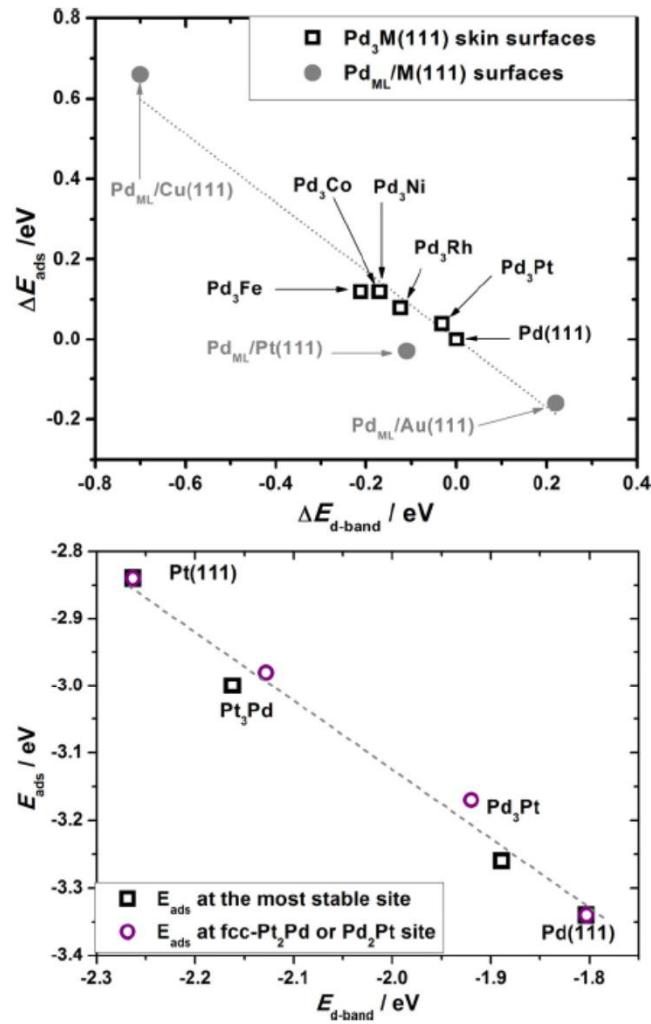
Adsorpcija i mobilnost adsorbata



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



Korelacija sa elektronskom strukturom



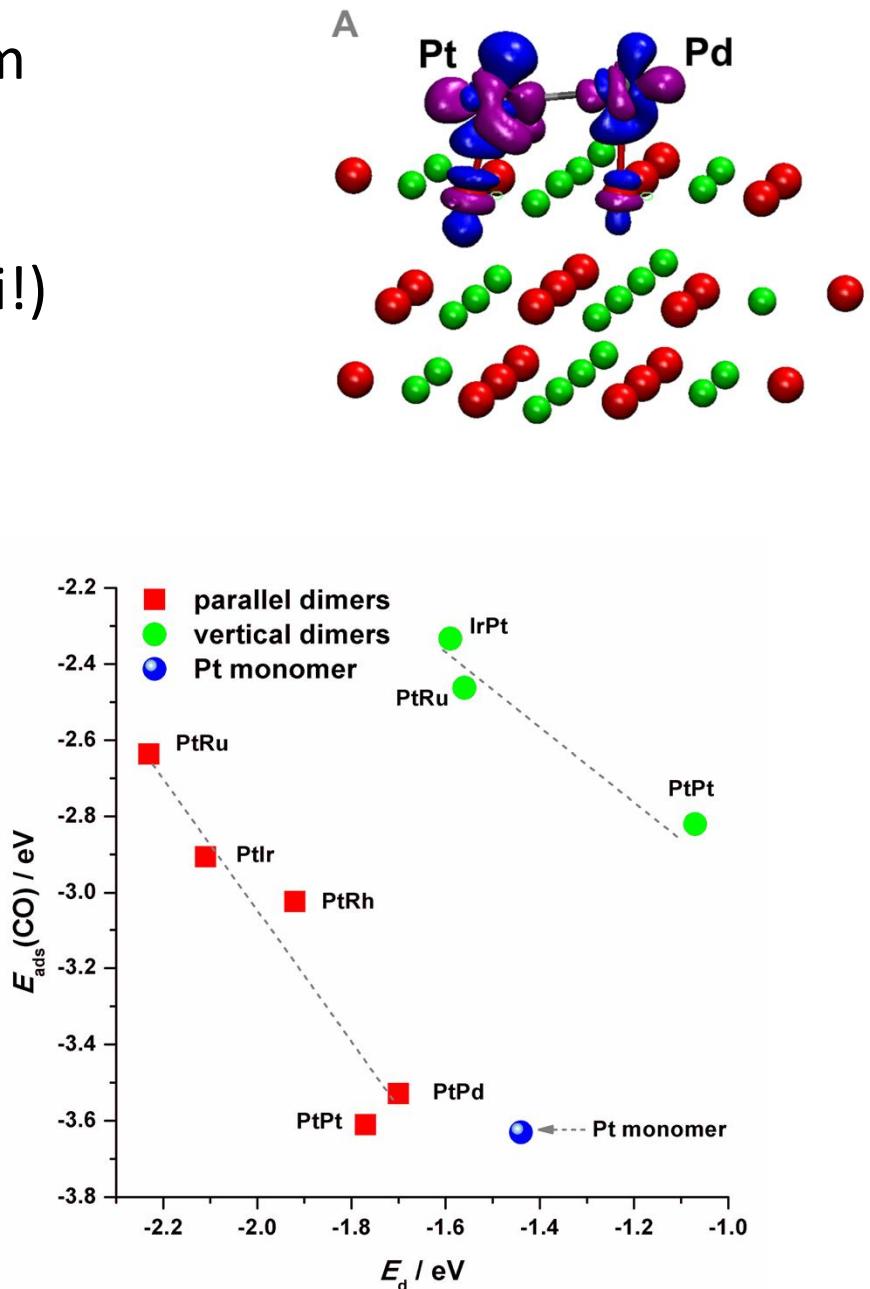
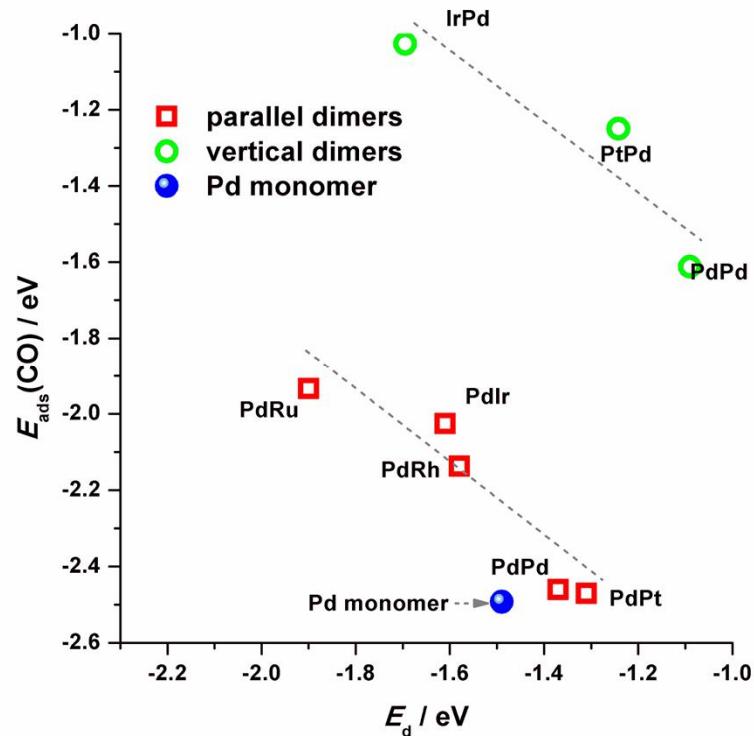
Electrochimica Acta 130 (2014) 453–463

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

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

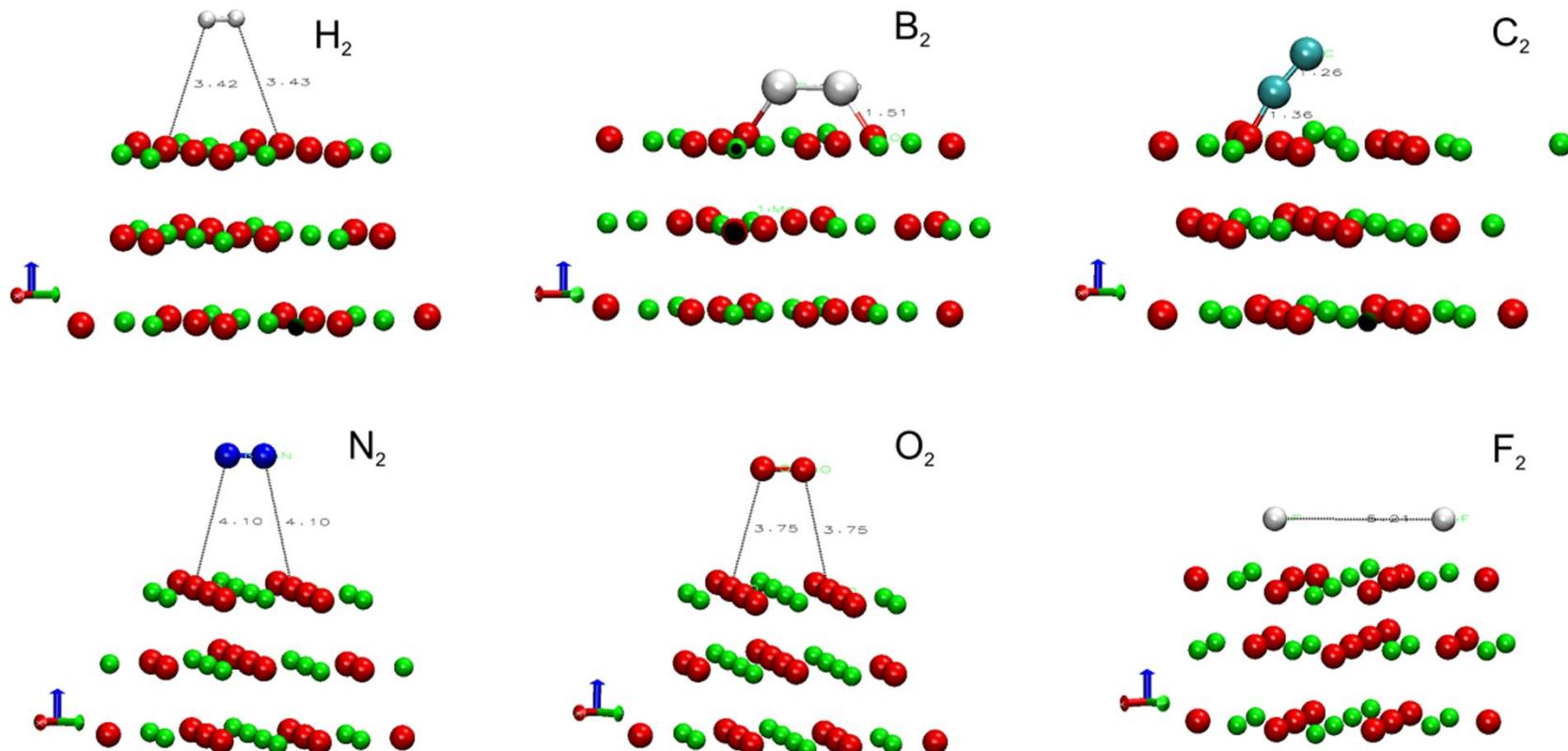
Nema jedinstvene teorije



Adsorpcija na oksidima – nema jedinstvene teorije

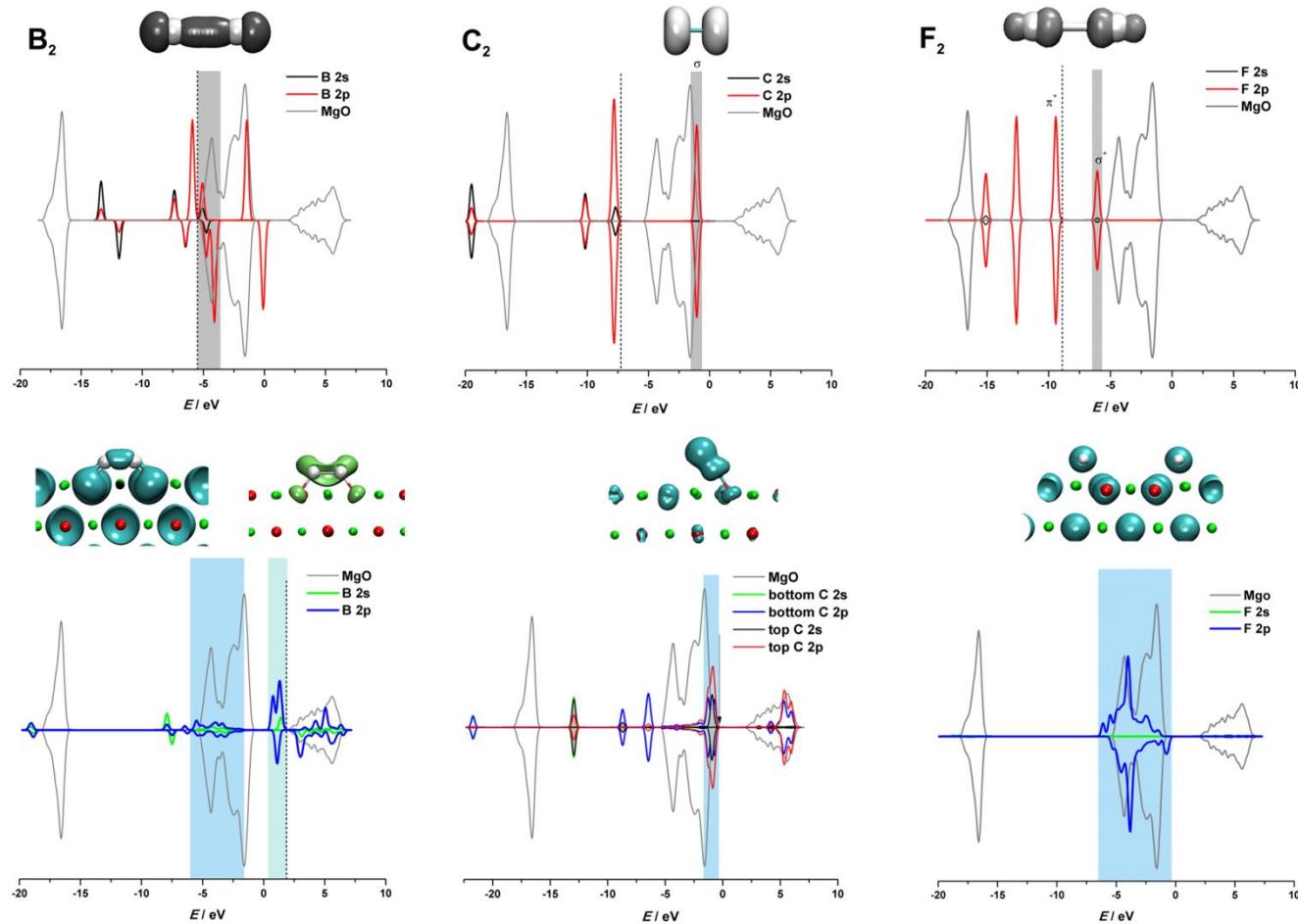
Primer: $X_2@MgO(001)$

Svojstva jonskih kristala!!!



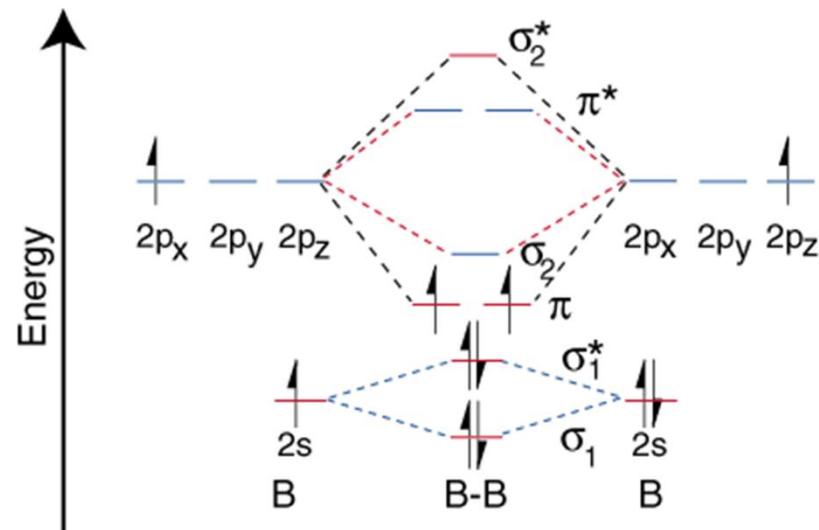
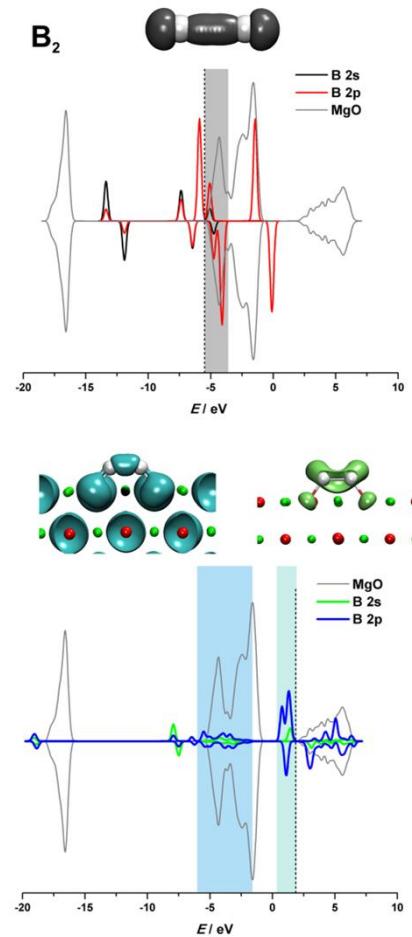
Adsorpcija na oksidima – nema jedinstvene teorije

Primer: C₂@MgO(001)



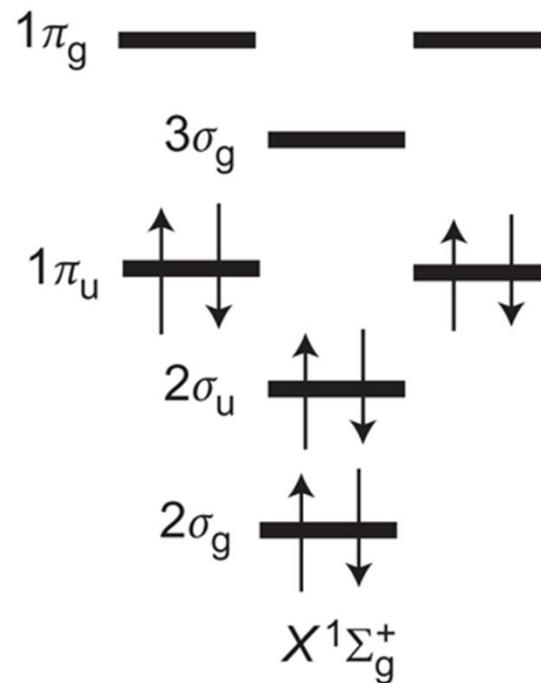
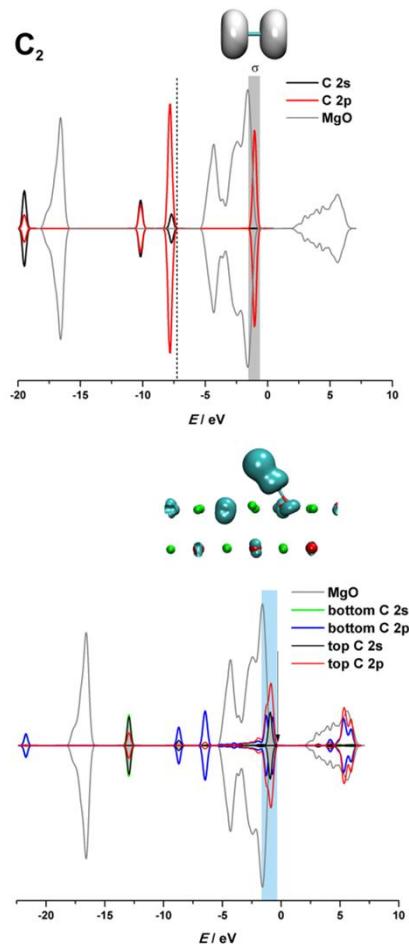
Adsorpcija na oksidima – nema jedinstvene teorije

Primer: $\text{B}_2@\text{MgO}(001)$



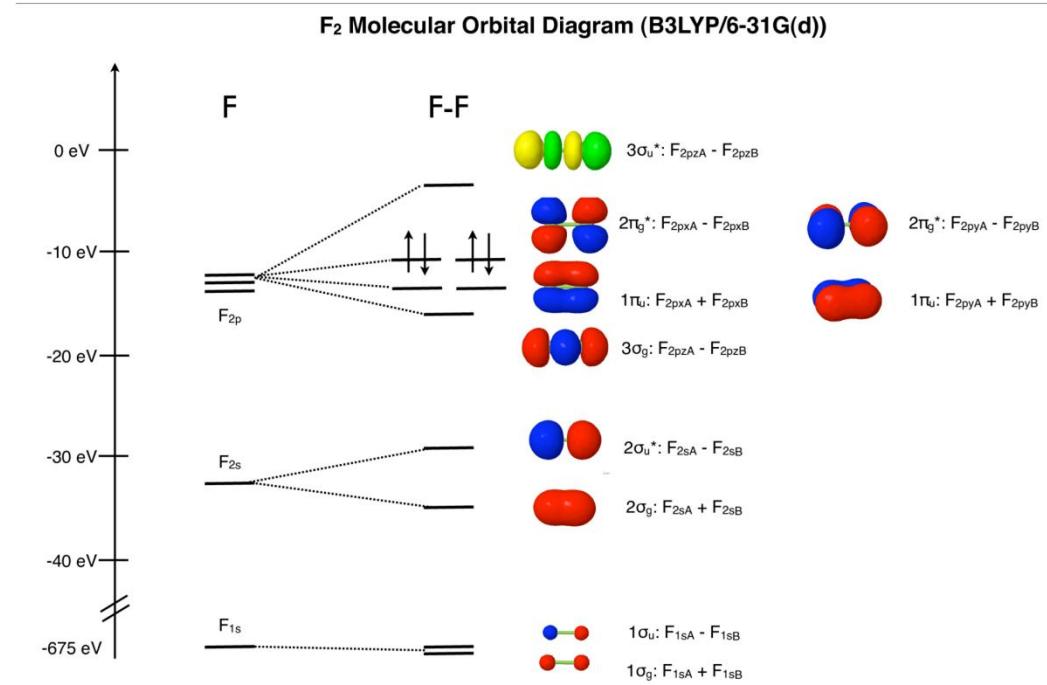
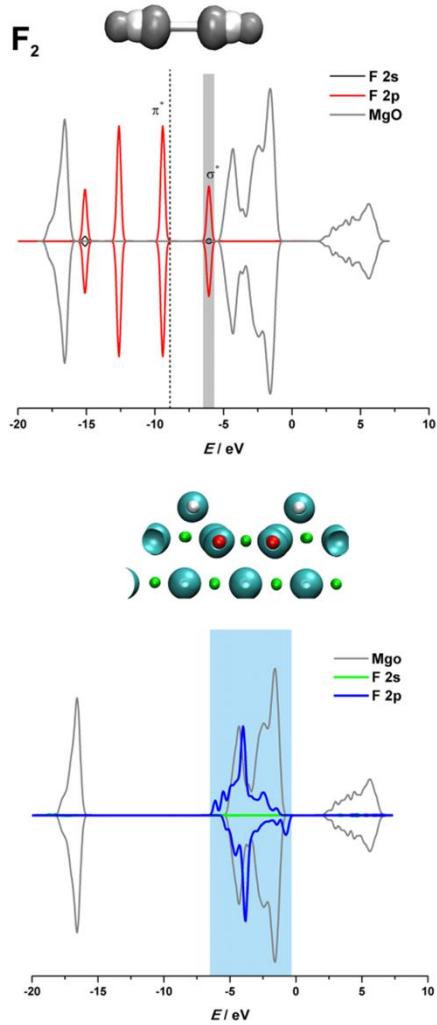
Adsorpcija na oksidima – nema jedinstvene teorije

Primer: C₂@MgO(001)

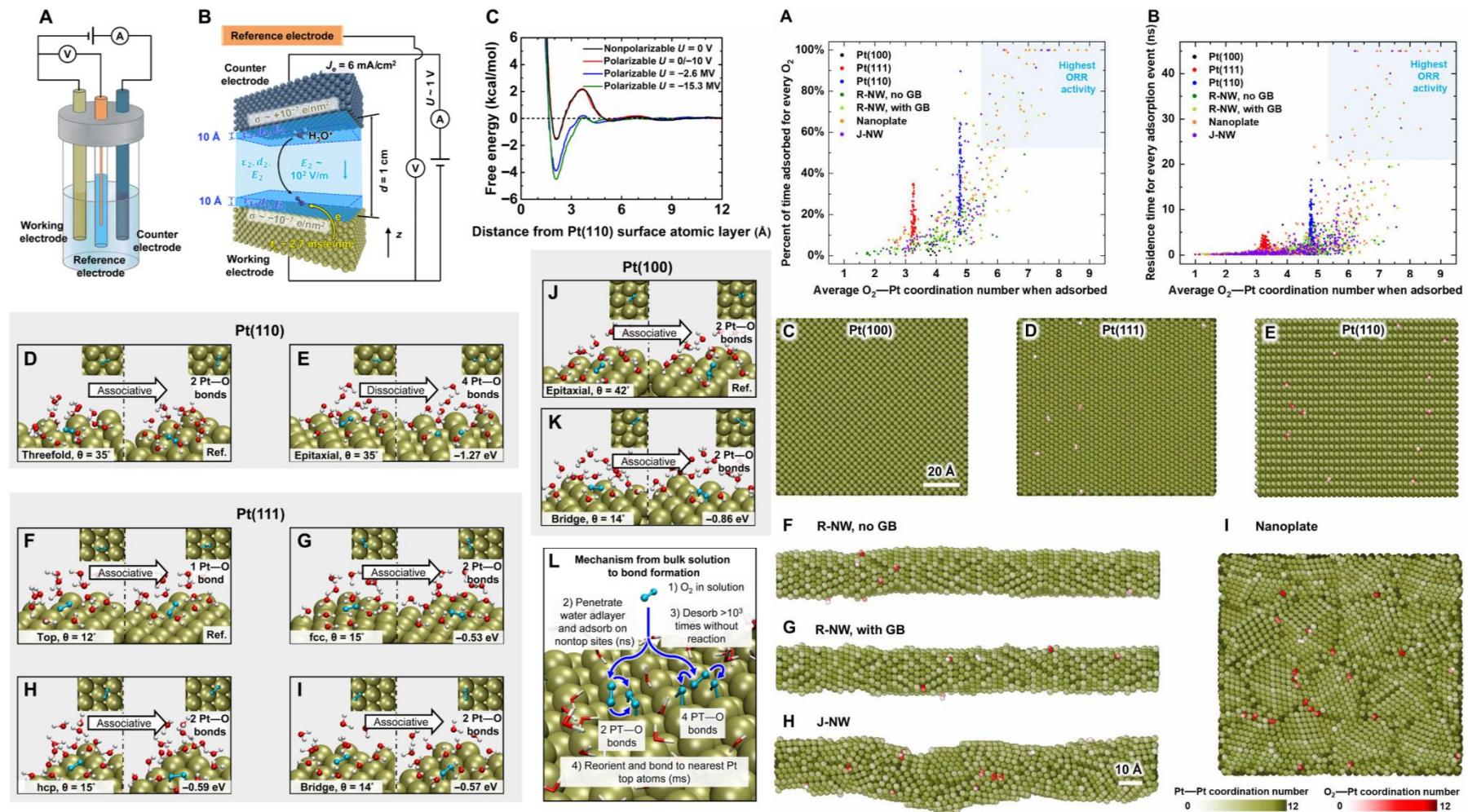


Adsorpcija na oksidima – nema jedinstvene teorije

Primer: $\text{F}_2@\text{MgO}(001)$



Adsorpcija i katalitička aktivnost



Adsorpcija i katalitička aktivnost

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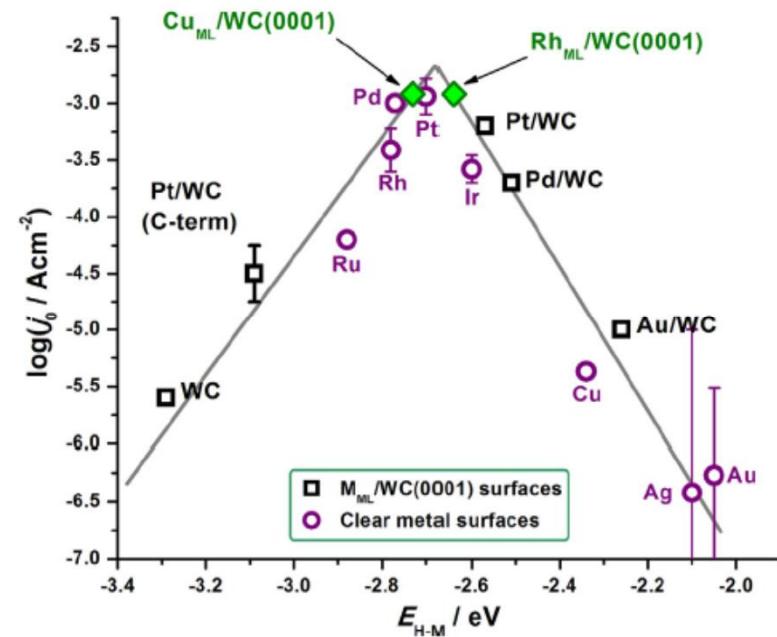
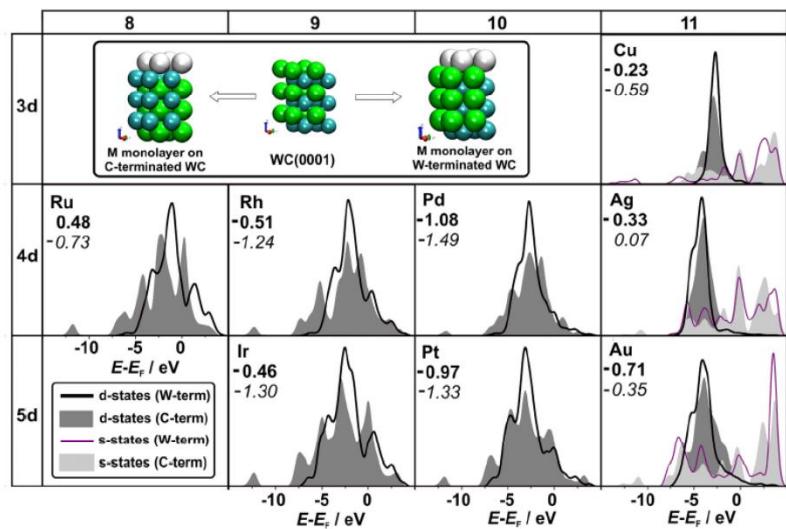


Fig. 3 – Volcano curve correlating hydrogen–metal binding energy (E_{H-M}) with corresponding experimentally determined HER activities of studied surface (expressed by $\log j_0$, j_0 in $A\text{ cm}^{-2}$) taken from Refs. [5,6,32,36,37], consolidating clean metal surfaces (\circ) and WC-based HER electrocatalysts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