First-Principles Study on the Design of Nickel based Bimetallic Catalysts for Xylose to Xylitol conversion

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S1. Calculation of d-band Center

The d-band center (ε_d) is calculated using the formula [1]:

$$\varepsilon_d = \frac{\int \rho E dE}{\int \rho dE}$$

where ρ is the density of d-states at each energy level E, and dE is the energy interval.

It is worthy to note that for the DOS calculation, an increase in the k point value is necessary to give improved results. Additional settings used for both the ionic and electronic relaxation in the INCAR file in VASP program are:

Ionic Relaxation	Electronic Relaxation

NSW = 0
IBRION = -1
#EDIFFG = -5E-02
	NCUT = 400.00 eV
	NELM = 90;
	NELMIN = 6
	EDIFF = 1E-06
	# RWIGS
	LWAVE = T
	LCHARG = T
	LAECHG = T
	# ICHARG = 11

ISMEAR = 1; SIGMA = 0.05

At the end of the electronic relaxation, a DOSCAR output file should be present in the directory. The DOSCAR output file contains the electronic DOS and integrated DOS of the surface as well as the projected DOS for each atom. Additional details about the DOSCAR output file can be found on the VASP wiki. With the DOSCAR output file and the split_dos script (present in the vtscripts), the DOSCAR file can be decomposed into the multiple DOS files (DOS1, DOS2…, DOSn) for each atom in the system numbered corresponding to each atom number in the POSCAR file. To obtain a single DOS file representing group of surface atoms, the sum_dos script (also present in the vtscripts) is used. The snapshots of Table 1S show the columns present in either of these file (i.e. DOSn or DOS.SUM.a.to.b).

Table 1S: Columns of DOSn or DOS.SUM.a.to.b file representing single or group of surface atoms.

Energy, E	Orbitals								dE (eV)	ρ	ρ*dE	ρ*E*dE
(eV)	s↑	s↓	p↑	p↓	d↑	d↓	sum↑	sum↓				
-10.1189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00000
-10.0589	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.9989	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.9389	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.8789	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.8189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.7589	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.6989	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.6389	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.5789	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.5189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.4589	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-9.3989	-0.0099	0.0099	-0.0014	0.0014	-0.0004	0.0004	-0.0117	0.0117	0.0600	-0.0008	0.0000	0.00043
-9.3389	0.0321	-0.0321	0.0045	-0.0045	0.0012	-0.0012	0.0378	-0.0378	0.0600	0.0025	0.0001	-0.00137
-9.2789	0.9040	-0.9040	0.1271	-0.1271	0.0346	-0.0346	1.0657	-1.0656	0.0600	0.0691	0.0041	-0.03847
-9.2189	0.2093	-0.2093	0.0294	-0.0294	0.0080	-0.0080	0.2467	-0.2468	0.0600	0.0160	0.0010	-0.00885
-9.1589	-0.0235	0.0235	-0.0033	0.0033	-0.0009	0.0009	-0.0278	0.0278	0.0600	-0.0018	-0.0001	0.00099
-9.0989	-0.0003	0.0003	0.0000	0.0000	0.0000	0.0000	-0.0003	0.0003	0.0600	0.0000	0.0000	0.00001
-9.0389	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.9789	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.9189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.8589	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.7989	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.7389	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.6789	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.6189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.5589	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.4989	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.4389	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.3789	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.3189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.2589	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.1989	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.1389	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.0789	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-8.0189	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0600	0.0000	0.0000	0.00000
-7.9589	-0.0003	0.0003	0.0000	0.0000	-0.0001	0.0001	-0.0004	0.0004	0.0600	-0.0001	0.0000	0.00006

Here, ρ = **d↑+ (-d↓)**

Finally, the d-band center, $\varepsilon_{d,}$ can be obtained as:

$$\varepsilon_d = \frac{\sum \rho E dE}{\sum \rho dE}$$

S2. Segregation Energy

The segregation energy, E_{seg}, is defined as the energy of moving an atom from the subsurface to the surface layer of a crystal [2]. It is defined as the difference in total energy between the segregated slab and the normal slab.

In this study, we assumed that if it is favorable for an atom to move from the interior to the surface, then it will be favorable for the whole similar atoms to migrate to the surface from the interior. Hence, we calculated the segregation energies for both vacuum and xylose adsorbed slabs. Figure 1S depicts the segregation pattern for an acyclic xylose adsorbed slab. Here, the E_{seg} can be calculated as $\mathbf{E_{seg} = E_b - E_a}$. The same calculation procedure was adopted for vacuum slabs.

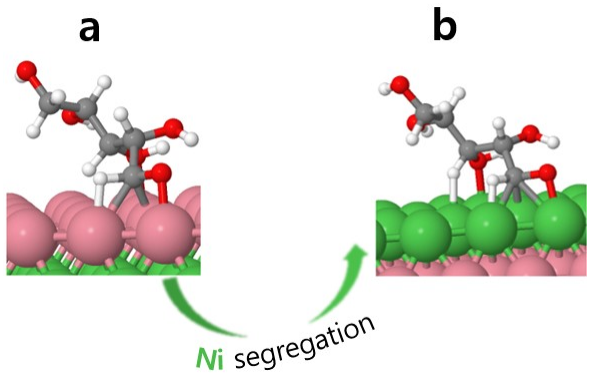
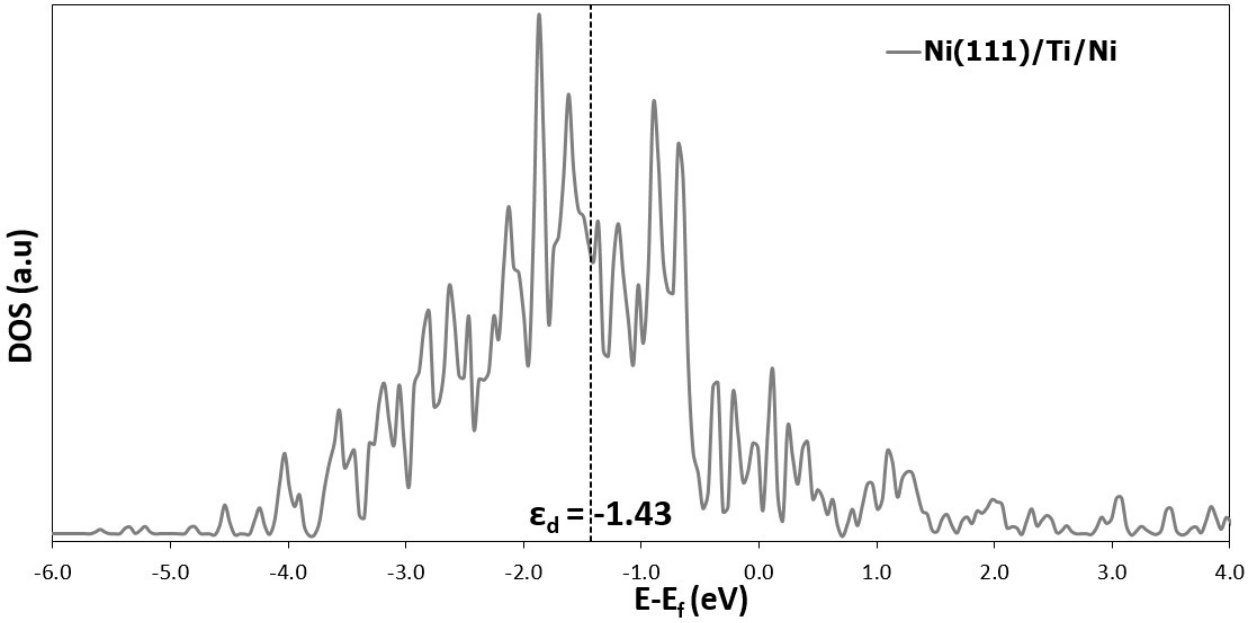
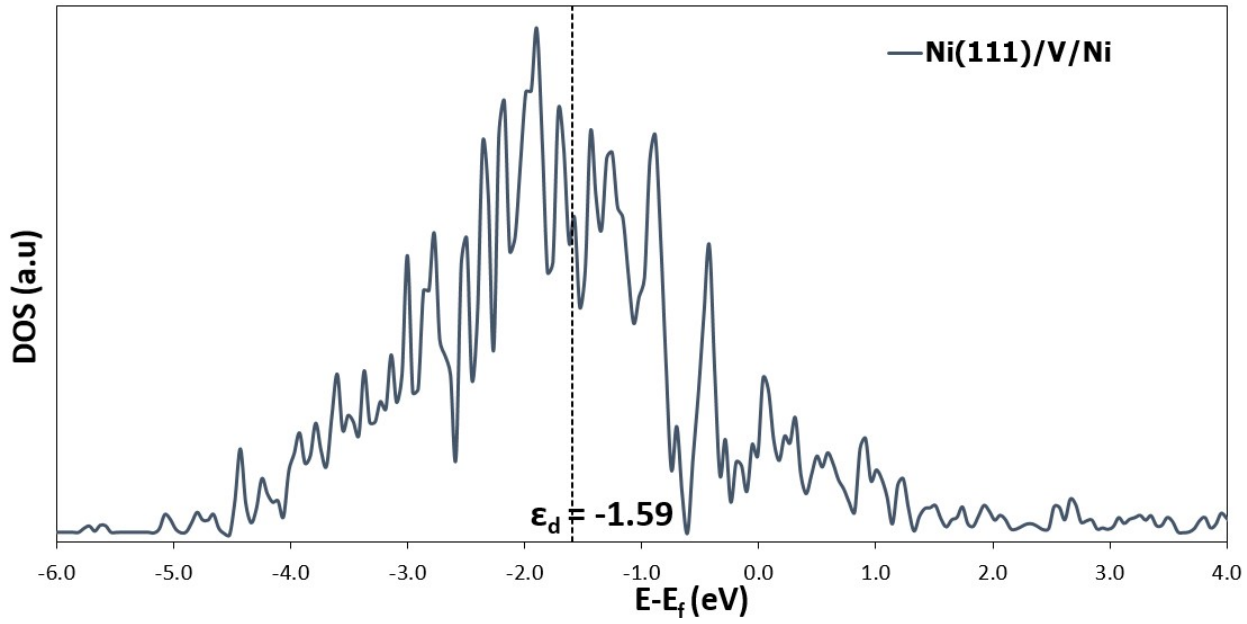


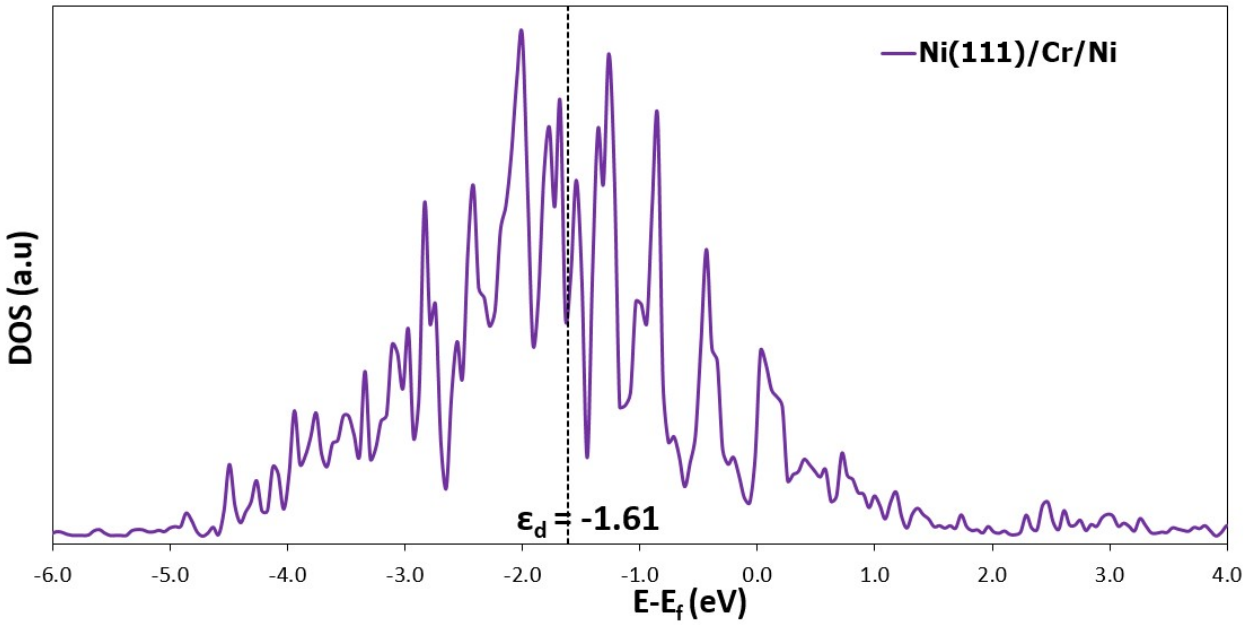
Fig. S1. Subsurface to surface segregation of Ni (111)/Co in acyclic xylose adsorbed condition.

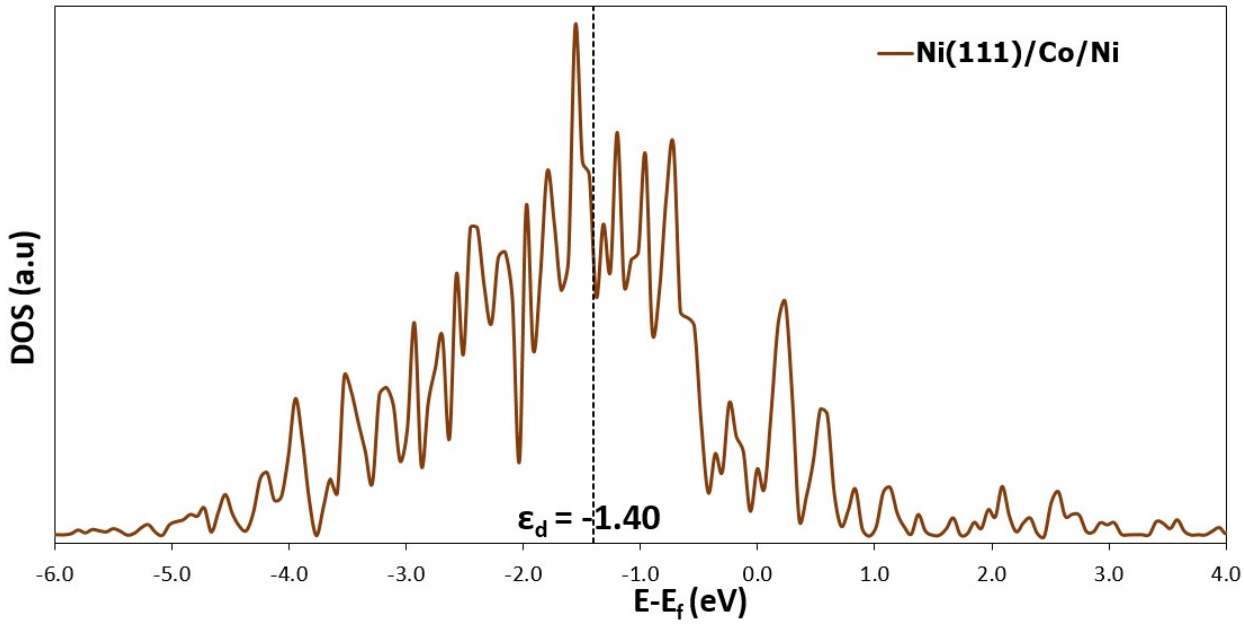
Table 2S. Comparison of cyclic xylose ($\mathbf{X_C}$) adsorption energies on 3 and 4 layers of 6 by 4 supercell. Bottom 2 layers of both models are fixed.

Surfaces	E_{ad1} (3-layers)	E_{ad2} (4-layers)
Ni (111)	-0.32	-0.28
Ni (111)/Co	-0.33	-0.32
Ni (111)/Cu	-0.27	-0.23
Ni (111)/Fe	-0.46	-0.54


Ni(111)/Ti/Ni
DOS (a.u)
ε_d = -1.43
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
E-E$_f$ (eV)


Ni(111)/V/Ni
DOS (a.u)
ε_d = -1.59
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
E-E$_f$ (eV)


Ni(111)/Cr/Ni
DOS (a.u)
ε_d = -1.61
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
E-E$_f$ (eV)


Ni(111)/Co/Ni
DOS (a.u)
ε_d = -1.40
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
E-E$_f$ (eV)

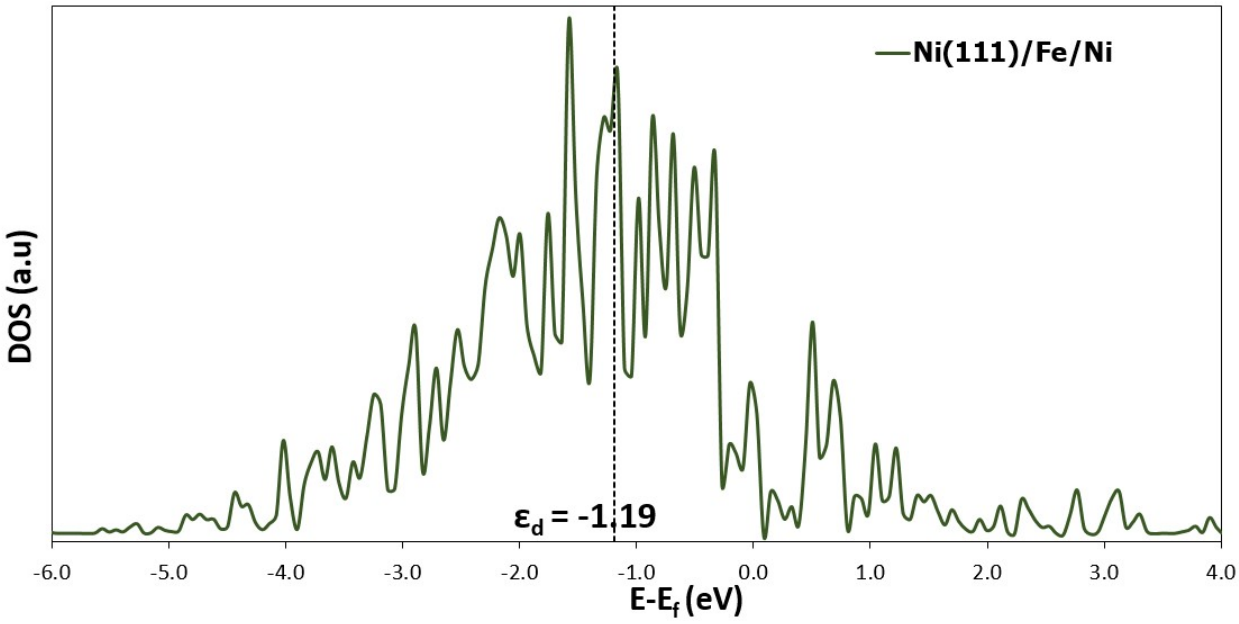


Fig. S2. Representation of partial density of states (DOS) of the d band surface atom(s) of Ni (111), Ni (111)/Co, Ni (111)/Cu, and Ni (111)/Fe, respectively. The 0 eV is the Fermi level position, and the dotted lines denote the d-band centers (ε_d). Refer to the supplementary page for the partial DOS of the other surfaces.

References

[1] I. Demiroglu, Z. Y. Li, L. Piccolo, R. L. Johnston, A DFT study of molecular adsorption on Au–Rh nanoalloys, Catalysis Science & Technology. 6 (2016) 6916–6931. https://doi.org/10.1039/C6CY01107A.

[2] Y. Ma, P.B. Balbuena, Pt surface segregation in bimetallic Pt3M alloys: A density functional theory study, Surface Science. 602 (2008) 107–113. https://doi.org/10.1016/j.susc.2007.09.052.