

Supporting Information (SI)

**Unravelling the Role of Oxophilic Metal in Promoting Deoxygenation of
Catechol on Ni-Based Alloy Catalyst**

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Table S1. DFT-calculated intrinsic and OH*-induced surface segregation energy (E_{segr}) for homogeneous NiFe(111) alloy and Fe@Ni(111) single-atom alloy.

M	Ni	Fe	Fe
Alloy	NiFe(111)	NiFe(111)	Fe@Ni(111)
E_{segr} (eV/M) ^a	-0.04	0.48	0.24
OH- E_{segr} (eV/M) ^b	0.37	0.36	-0.47

^a $E_{\text{segr}} = [E(\text{M/slab}) - E(\text{NiFe(111)/slab})]/n$, where n is the number of M atoms (either Ni or Fe) in the second layer segregated to the upmost top layer, M/slab represents a slab that is completely covered with M atoms (either Ni or Fe) in the upmost top layer while the second layer is otherwise made up of either Fe or Ni atoms. The third and the fourth layers remain the same as homogeneous NiFe(111) alloy, i.e., NiFe(111)/slab. For Fe@Ni(111), only one Fe atom is involved in the upmost top layer and the second layer. Negative/positive E_{segr} denotes segregation/anti-segregation tendency of M.

^bWith full coverage of OH*.

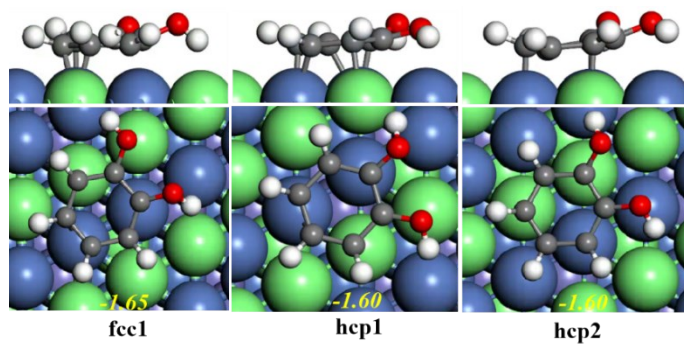
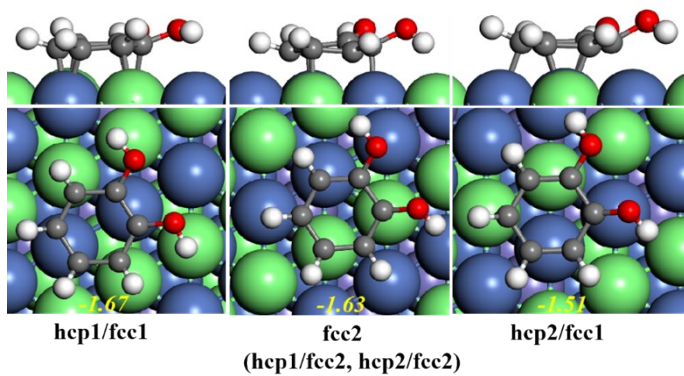
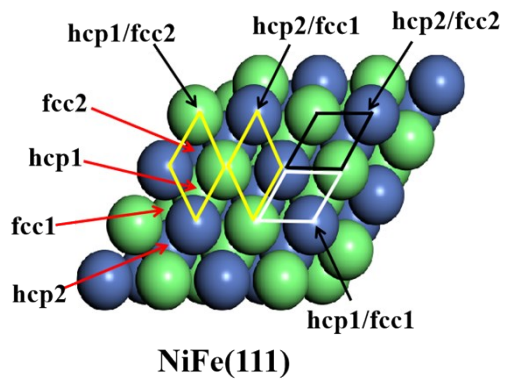
Table S2. DFT-calculated binding energy (BE) for surface species adsorbed on three Ni-based (111) surfaces.

Surface Species	Ni(111)	Fe@Ni(111)	NiFe(111)
	BE (eV)		
*H ^a	-0.56	-0.53	-0.63
*H ^b	-0.53	-0.51	-0.61
*OH ^c	-3.37	-3.51	-3.80
*OH	-3.41	-3.55	-3.87
*H ₂ O	-0.31	-0.43	-0.38
*H ₂ O	-0.38	-0.50	-0.47
*C ₆ H ₄ (OH) ₂	-0.70	-0.72	-0.63
*C ₆ H ₄ (OH) ₂	-1.71	-1.74	-1.67
*C ₆ H ₅ (OH)	-0.92	-0.98	-0.89
*C ₆ H ₅ (OH)	-1.79	-1.86	-1.79

^aBE(H) = $E(*\text{H/slab}) - E(\text{slab}) - 0.5E(\text{H}_2)$

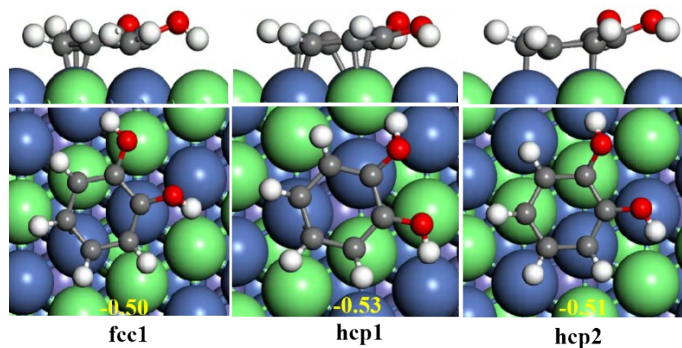
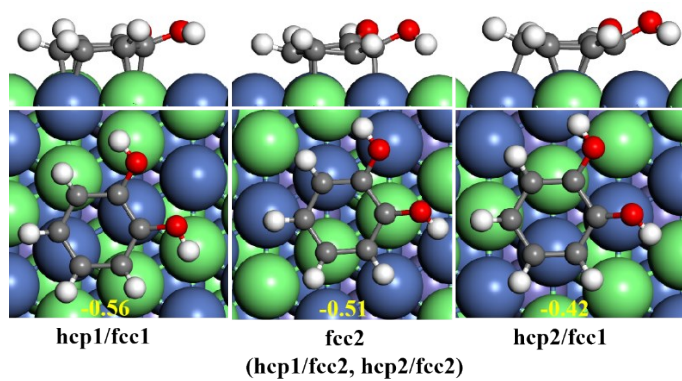
^bItalic number: calculated using optB88-vdW functional; Plain number: calculated using PBE exchange-correlation functional.

^cBE(OH) = $E(*\text{OH/slab}) - E(\text{slab}) - E(\text{OH})$



(a)

(b)



(c)

Figure S1. (a) Adsorption sites (rhombus) for aromatic adsorbates on homogeneous NiFe(111) alloyed surface, where 1 and 2 represent the number of Fe atoms in one of the threefold hollow sites, *fcc* or *hcp*. (b) Adsorption configurations of catechol on NiFe(111) calculated using optB88-vdW functional. (c) Adsorption configurations of catechol on NiFe(111) calculated using PBE functional. Adsorption energy (in eV) was labeled.

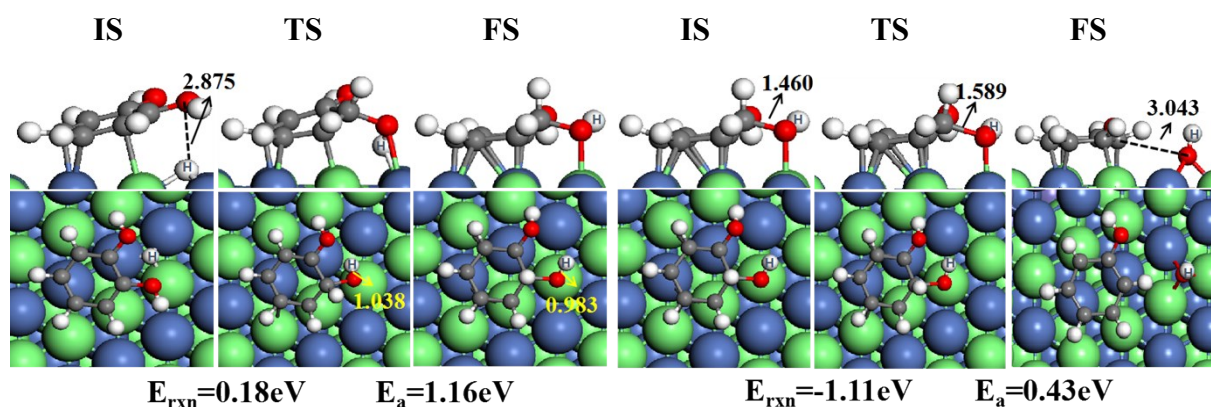


Figure S2. Geometrical configurations of initial state (IS), transition state (TS) and final state (FS) along TH & DO path on NiFe(111). The transition state of TH was located in a concerted way that the adsorbed *H from dissociated H₂ on NiFe(111) attacks hydroxyl-O of catechol meanwhile hydroxyl-H is being transferred to carbonyl-C in the phenyl ring.