Supporting Information

Influence of Promoters (Fe, Mo, W) on the Structural and Catalytic Properties of Ni/BEA for Guaiacol Hydrodeoxygenation

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17 pages, 11 figures (Figure S1-S11), and 13 tables (Table S1-S13)

1. Catalyst characterization

The X-ray diffraction patterns of calcined and reduced catalysts were determined using a Phillips X'pert Pro diffractometer with Cu kα radiation. The XRD patterns were collected in the range of 2θ=5-100 °. SEM images of the reduced catalysts were captured using a Zeiss sigma VP Field Emission-SEM with a secondary electron (SE) detector. Transmission electron microscopy (TEM) imaging was performed with a JEOL JEM-1200EXII TEM (200 kV) microscope, equipped with an EDXS spectrometer. The samples for TEM analysis were ultrasonically dispersed in ethanol. One drop of the suspension was deposited on copper grids coated with carbon films. The contents of Ni, Fe, W, Mo, Si and Al over the prepared catalysts were determined by X-ray fluorescence multi-elemental analyses (XRF).

Nitrogen adsorption measurements were conducted in a Micromeritics Gemini Surface Area Analyser at -196 °C. Prior to nitrogen adsorption, the sample was vacuumed overnight at 200 °C. The *t*-plot and Barrett-Joyner-Halenda (BJH) models were used to estimate micro and mesopore volume, as well as pore size distribution. The concentration of acid sites was determined by temperature-programmed desorption (TPD) of ammonia, using an apparatus described in detail elsewhere [1].

 H_2 temperature-programmed reduction (H_2 -TPR) was carried out in a home-made instrument to investigate the reducibility of catalyst. 200 mg catalyst was loaded in a quartz tube. The catalyst was first activated in air (50 mL/min) at 500 °C for 30 min to remove the water then cooled to 25 °C, followed by reduction in a 2.04 vol% H_2 /Ar flow (50 mL/min) using a heating rate of 10 °C/min. The hydrogen consumption was determined by a thermal conductivity detector (TCD). A trap containing dry ice was placed between the reactor and TCD to remove water.

H₂-temperature-programmed-desorption (H₂-TPD) experiments were carried out in an apparatus described in detail elsewhere [1]. 0.2 g catalyst was used and reduced in a pure H₂ (50 mL/min) at 550 °C for 4 h, then the sample was cooled to 50 °C and saturated with 10 mbar H₂. The H₂ desorption pattern was obtained by heating from 50 °C to 500 °C with a heating rate of 10 °C/min. The desorbed H₂ was detected by a mass spectrometer.

Metal dispersion of catalysts was measured by volumetric chemisorption. All samples were pre-treated by pure H₂ at 450 °C for 90 min with a H₂ flow of 100 mL/min. The chemisorption of carbon monoxide was performed at 35 °C in a pressure range between 30 and 90 mbar, and the gas adsorbed on the catalyst was calculated based on the ideal gas law and assume a stoichiometry of CO/M (Ni, Mo W and Fe) =1/1. Based on the volume of chemisorbed CO,

the metal particles dispersion (D), specific surface area (SA) and average metal particles size (d) were calculated using Eqs.1-3 [2, 3].

$$D = \frac{N_S}{N_t} \times 100\% = \frac{SF \cdot M_W \cdot n \cdot 10^2}{W \cdot wt\%}$$
(1)
$$SA\left(\frac{m^2}{g}\right) = \frac{SF \cdot n \cdot \sigma \cdot N_A}{wt\% \times W}$$
(2)
$$d (nm) = \frac{\varphi \cdot V_M \cdot S_M^{-1}}{D} = \frac{\varphi \cdot M_W \cdot \sigma}{D \cdot \rho \cdot N_A} = \frac{6000}{SA \cdot \rho}$$
(3)

Where N_s is the mole of accessible metal, N_t represents the mole of total metal content, SF is stoichiometry factor CO/M (Ni, Mo W and Fe) =1/1, M_w is formula weight of the particle (g/mol), n is the mole of active gas adsorbed, wt% represents weight% metal, W is the total weight of sample, σ is the atomic cross-sectional area of metal (m²/atom), N_A is the Avogadro number, φ is a constant which reflects particle shape (e.g. φ is 6 for spheres and cubes), V_M is the volume per metal atom, S_M is the average surface area of metal particles per surface metal atoms, and ρ is the metal particle density (g/cm³).

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer (ESCALAB250Xi) at room temperature using mono-chromated Al K α (energy 1486.6 eV) radiation. The adventitious hydrocarbon located at 284.8 eV was used to calibrate binding energy. The spectrometer was pre-calibrated using Au 4f⁷ (83.96 eV), Ag 3d⁵ (368.21 eV), and Cu 2p³ (932.62 eV).

2. Catalyst performance assessment

Catalytic hydrodeoxygenation (HDO) of guaiacol was performed in a continuous-flow reactor. 50 mg of calcined catalyst was charged in the centre of the reaction tube and fixed in place with quartz wool. Prior to reaction, the calcined catalyst was reduced under a pure H₂ gas stream (50 mL/min) at 550 °C for 4 h, following which the catalyst was cooled to 230 °C and the pure H₂ (120 mL/min) was fed into the reactor and maintained at 4.0 MPa. For the HDO reaction, pure guaiacol was pumped into the reactor with a weight hourly space velocity (WHSV) of 3.12 min⁻¹.

In order to evaluate the catalyst's hydrogenation activity, hydrogenation of toluene was performed in the aforementioned flow reactor using 50 mg of reduced catalyst at 230 °C under

4.0 MPa of hydrogen. Besides, cyclohexanol was also employed as feed to test the catalyst deoxygenation activity.

The gas products were analysed online using a Varian 490-GC micro gas chromatograph. The liquid products were collected by a cold trap and analysed using an Agilent 6890 series GC with an Agilent 5973N detector, equipped with a DB-5MS column (30 m length, 0.25 mm ID, 0.25 μ m film thickness).



Figure S1. Nitrogen adsorption isotherms for the pre-reduced samples



Figure S2. NH $_3$ -TPD profiles of the pre-reduced BEA supported Ni, Ni-Mo, Ni-Fe, Ni-W catalysts

Catalyst	Acid concentration
	(mmol/g _{cat})
Ni/BEA	0.80
Ni-Mo/BEA	0.75
Ni-W/BEA	0.74
Ni-Fe/BEA	0.71

Table S1 Acid concentrations of the pre-reduced catalysts

The acid concentrations were determined by quantifying the desorbed NH₃ with NH₃-TPD



Figure S3. XRD pattern of reduced 6.0 wt% Ni- 1.8 wt% Fe/BEA



(b)



Figure S4. TEM images of (a) Ni-Fe/BEA, (b) Ni-Mo/BEA and (c) Ni-W/BEA





Figure S5. EDX mappings of (a) Ni-Fe/BEA, (b) Ni-Mo/BEA, and (c) Ni-W/BEA



(C)				(d)			
			-				
100 100							
100 nm	Mag = 100.00 K X Width = 3.019 μm WD = 8.0 mm	Signal A = NTS BSD Signal B = NTS BSD Signal = 1.000	Gun= 5. Chm=1. Sys= 1.	200 nm	Mag = 100.00 K X Width = 3.019 μm WD = 7.9 mm	Signal A = NTS BSD Signal B = NTS BSD Signal = 1.000	Gun= 9 Chm=2 Sys= 2.

Figure S6. SEM images of pre-reduced (a) Ni/BEA, (b) Ni-Mo/BEA, (c) Ni-Fe/BEA and (d) Ni-W/BEA

Si	Al	0	Ni	Fe	Мо	W
24.7	1.6	72.7	0.97	-	-	-
23.9	1.5	73.3	1.17	0.14	-	-
23.6	1.5	73.6	1.15	-	0.14	-
24.4	1.7	72.8	1.00	-	-	0.1
	Si 24.7 23.9 23.6 24.4	Si Al 24.7 1.6 23.9 1.5 23.6 1.5 24.4 1.7	SiAlO24.71.672.723.91.573.323.61.573.624.41.772.8	SiAlONi24.71.672.70.9723.91.573.31.1723.61.573.61.1524.41.772.81.00	SiAIONiFe24.71.672.70.97-23.91.573.31.170.1423.61.573.61.15-24.41.772.81.00-	SiAlONiFeMo24.71.672.70.9723.91.573.31.170.14-23.61.573.61.15-0.1424.41.772.81.00

Table S2 Surface atomic element percentage (based on XPS)

Table S3 Electron configuration of Ni, Fe, Mo and W

Element	Electron configuration	Allen electronegativity [4]
Ni	[Ar] 3d ⁸ 4s ²	1.88
Fe	[Ar] 3d ⁶ 4s ²	1.80
Мо	[Kr] 4d⁵ 5s¹	1.47
W	[Xe] 4f ¹⁴ 5d ⁴ 6s ²	1.47

Table S4 XPS data of pre-reduced Ni-based samples

Sample	Ni2p _{3/2}	SAT ^a	$\Delta E_{2p3/2}^{b}$
		(Ni2p _{3/2})	·
Ni/BEA	854.8	861.3	6.5
	858.3	864.5	6.2
Ni-Fe/BEA	854.8	861.5	6.7
	858.0	864.3	6.3
Ni-Mo/BEA	854.8	860.8	6.0
	858.1	864.0	5.9
Ni-W/BEA	854.8	861.7	6.9
	858.3	865.1	6.8

^a SAT: satellite of main peak

^b Energy difference between satellite and main peak.



Figure S7. H₂-TPR profiles of BEA supported Ni, Ni-Mo, Ni-Fe, Ni-W catalysts

3. Computational details.

3.1. Methods.

Spin-polarized density functional theory (DFT) calculations were carried out by using the Vienna *ab initio* simulation package (VASP) [5, 6]. The projected augmented wave method (PAW) [7] was applied, the electron exchange and correlation energies were treated using the generalized gradient approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) functional [8, 9]. The cutoff energy was set up to 400 eV. Geometry optimization was converged until the energy difference was lower than 10⁻⁵ eV, and the forces acting on atoms were lower than 0.02 eV/Å.

3.2. Models.

The bulk cells of metallic Ni, Fe, Mo and W were optimized, and the calculated average

energies per atom were used as energy references in following discussion. The k-point grid used in this calculation and the lattice parameters after optimization are listed in Table S5. Three models, namely bulk alloy model (Ni_3M_1 , Ni_4M_1 , Ni_5M_1), surface alloy model ($M_{surf-alloy}/Ni(111)$) and interface model (M_{1ML}/Ni (111)), were used to simulate various Ni-M (M=Fe, Mo, W) system morphology.

Metal	k-point grid	Lattice parameters
Ni	$9 \times 9 \times 9$	<i>a</i> = b = c= 3.509 Å
Fe	11 × 11 × 11	a = b = c= 2.824 Å
Мо	10 × 10 × 10	<i>a</i> = b = c= 3.160 Å
W	9 × 9 × 9	<i>a</i> = b = c= 3.185 Å
Ni Fe Mo W	9 × 9 × 9 11 × 11 × 11 10 × 10 × 10 9 × 9 × 9	a = b = c= 3.509 Å a = b = c= 2.824 Å a = b = c= 3.160 Å a = b = c= 3.185 Å

 Table S5 The k-point grid used in the calculation and the lattice parameters after optimization of Ni/Fe/Mo/W metals

3.2.1. Bulk alloy model (Ni₃M₁/Ni₄/M₁/Ni₅M₁)

(1) Ni_3M_1/Ni_4M_1 models were designed to simulate the alloy with considerably high content of doping metal. The structures of Ni_3Fe_1 , Ni_4Mo_1 and Ni_4W_1 were obtained refer to previous experimental works [10-12]. A 9 × 9 × 9 Monkhorst–Pack k-point grid was used to calculate Ni_3Fe_1 and 7 × 7 × 9 Monkhorst–Pack k-point grid was used to calculate Ni_4Mo_1 and Ni_4W_1 , with the optimized structures displayed in Figure S8.

(2) Ni_5M_1 model was employed to simulate the alloy with high Ni/M atomic ratio. The structures of Ni_5M_1 were based on a p (3 × 2) supercell with 24 Ni atoms. A total of 21 Ni_5Fe_1 structures were designed by randomly replacing four Ni atoms with Fe atoms. A 3 × 5 × 9 Monkhorst– Pack k-point grid was applied to calculate this kind of model. The structure with the lowest energy was selected as the Ni_5Fe_1 alloy model and was used to construct Ni_5Mo_1 and Ni_5W_1 alloy models by replacing Fe atoms with Mo or W atoms (Figure S8).

The formation energy (E_f) of Ni_xM₁ (x=3, 4, 5) models is calculated using:

 $E_{\rm f} = 1/n E_{\rm NixM1} - E_{\rm M/per atom} - xE_{\rm Ni/per atom}$

Where E_{NixM1} is the total energy of the Ni_xM₁ bulk, *n* is the number of M (M=Fe, Mo, W) atoms in the Ni_xM₁ bulk cell, $E_{M/per atom}$ is the average energy per atom of the metallic Fe/Mo/W bulk, and $E_{Ni/per atom}$ is the average energy per atom of the metallic Ni bulk.



3.2.2. Surface alloy model

 $M_{surf-alloy}/Ni(111)$ model represents the catalysts with low content of doping metal, which could form surface alloy. A four-layered p(3 × 3) supercell was chosen to simulate the Ni(111) surface, where the top two layers were allowed to relax and the bottom two layers were fixed in their bulk positions. One surface Ni atom was substituted by one M (Fe/Mo/W) atom (as shown in Figure S9). The surface Ni/M ratio (8) is close to the experimental observation (Table 1). The vacuum layer thickness between periodically repeated slabs was set to 12 Å to avoid interactions between slabs. A 5 × 5 × 1 Monkhorst–Pack k-point grid was used for sampling the Brillouin zone of the surface. The formation energy (E_f) of $M_{surf-alloy/Ni(111)}$ model is calculated using:

$$E_{f} = E_{M-surf-alloy/Ni(111)} + E_{Ni/per atom} - E_{M/per atom} - E_{Ni(111)}$$

Where $E_{M-surf-alloy/Ni(111)}$ is the total energy of the $M_{surf-alloy}/Ni(111)$ model, and $E_{Ni(111)}$ is the total energy of the clean Ni(111) surface.



Figure S9. The structure of surface-alloy model

3.2.3. Interface model

 $M_{1ML}/Ni(111)$ model represents the Ni(111) surface with one monolayer adsorption of the doping metals. This model was utilized to simulate the case that Ni and the doping metal do not form alloy but construct an interface. A four-layered $p(2 \times 2)$ supercell and a 7 × 7 × 1 Monkhorst–Pack k-point grid was employed for this model. Other simulating parameters were the same with above surface alloy model. Both fcc and hcp adsorption sites were checked for single metal atom adsorption (as displayed in Figure S10). The adsorption energy (E_{ads}) is calculated using:

 $E_{\text{ads-atom}} = E_{\text{M/Ni(111)}} - E_{\text{M-atom}} - E_{\text{Ni(111)}}$ or $E_{\text{ads-bulk}} = E_{\text{M/Ni(111)}} - E_{\text{M/per atom}} - E_{\text{Ni(111)}}$

where $E_{M/Ni(111)}$ is the total energy of the slab with single adsorbed doping metal atom, $E_{Ni(111)}$ is the total energy of the Ni(111) slab and E_{M-atom} is the total energy of single metal atom. It is noticed that the fcc adsorbed slab is slightly thermodynamic preferred compared to hcp adsorbed slab (Table S6). Therefore, the model with one monolayer coverage M atoms at fcc phase was used for further discussion (Figure S10). The adsorption energy of this model is calculated using:

 $E_{\text{ads-atom}} = E_{\text{M-1ML/Ni(111)}} - nE_{\text{M-atom}} - E_{\text{Ni(111)}}$ or $E_{\text{ads-bulk}} = E_{\text{M-1ML/Ni(111)}} - nE_{\text{M/per atom}} - E_{\text{Ni(111)}}$

where $E_{M-1ML/Ni(111)}$ is the total energy of the slab with one monolayer adsorbed doping metals, and *n* is the number of doping metal atoms (*n* = 4 in this work). The formation/adsorption energies of above-mentioned models with respect to the average energy per atom of the metallic bulk are summarized in Table S7. Bader charge analyzing results are shown in Table S8 for alloy models and Table S9 for adsorption models.

Model	$E_{\rm ads-atom}$ (eV)	$E_{\rm ads-bulk}$ (eV)
Fe(fcc)/Ni(111)	-4.00	1.03
Fe(hcp)/Ni(111)	-3.97	1.07
Fe(1ML)/Ni(111)	-19.39	0.75
Mo(fcc)/Ni(111)	-3.51	2.80
Mo(hcp)/Ni(111)	-3.48	2.84
Mo(1ML)/Ni(111)	-21.28	3.98
W(fcc)/Ni(111)	-5.08	3.30
W(hcp)/Ni(111)	-5.06	3.31
W(1ML)/Ni(111)	-27.52	5.98

Table S6 The adsorption energies of Fe/Mo/W single atom or one monolayer on Ni (111) surface with respect to the energy of single atom ($E_{ads-atom}$) or the metallic bulk ($E_{ads-bulk}$).



Figure S10. The structures of adsorption models

Ni _{3/4} M ₁	E _f	Ni ₅ M ₁	E _f	M _{surf-alloy} /Ni(111)	E _f	M _{1ML} /Ni(111)	$E_{ads-bulk}$
Ni₃Fe₁	-0.35	Ni₅Fe₁	-0.33	Fe _{surf-alloy} /Ni(111)	-0.25	Fe _{1ML} /Ni(111)	0.75
Ni ₄ Mo ₁	-0.44	Ni ₅ Mo ₁	-0.05	Mo _{surf-alloy} /Ni(111)	0.37	Mo _{1ML} /Ni(111)	3.98
Ni_4W_1	-0.55	Ni_5W_1	-0.18	W _{surf-alloy} /Ni(111)	0.39	W _{1ML} /Ni(111)	5.98

Table S7 The formation energy $(E_f \text{ eV})$ of all models

Table S8 The average bader charge (q, e) for Ni and promoters (Fe, W, Mo) in alloy models

Ni _{3/4} M ₁	q _{Ni}	$q_{_{\mathrm{M}}}$	Ni ₅ M ₁	9 _{Ni}	$q_{_{\mathrm{M}}}$	M _{surf-alloy} /Ni(111)	$\boldsymbol{q}_{_{\mathrm{Ni}}}$	$q_{_{\rm M}}$
Ni ₃ Fe ₁	-0.15	0.44	Ni_5Fe_1	-0.08	0.40	Fe _{surf-alloy} /Ni(111)	-0.01	0.38
Ni₄Mo₁	-0.16	0.65	Ni ₅ Mo ₁	-0.13	0.64	Mo _{surf-alloy} /Ni(111)	-0.01	0.53
Ni_4W_1	-0.18	0.71	Ni_5W_1	-0.14	0.71	W _{surf-alloy} /Ni(111)	-0.01	0.54

The negative value indicates metal is electron acceptor, and the positive value represents the metal is electron donor.

Table S9 The average bader charge (q, e) for Ni and other metals in adsorption models

M/Ni(111)	q _{Ni}	$q_{_{ m M}}$	M _{1ML} /Ni(111)	9 _{Ni}	$q_{_{ m M}}$
Ni-111-Fe-fcc	-0.02	0.34	Ni-111-Fe-ML	-0.02	0.08
Ni-111-Mo-fcc	-0.02	0.41	Ni-111-Mo-ML	-0.03	0.13
Ni-111-W-fcc	-0.02	0.38	Ni-111-W-ML	-0.03	0.12

The negative value indicates metal is electron acceptor, and the positive value represents the metal is electron donor.

Table S10	Hydrodeoxy	genation of	f guaiacol	with low	WHSV ^[a]
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Catalyst	X-guaiacol (%)	Y-cyclohexane (%)	r- _{cyclohexane} (mol ·min ⁻¹ ·g ⁻¹ ·10 ⁻
(HBEA)			4)
Ni	19.2	5.1	7.9
Ni-Mo	24.1	7.7	11.9
Ni-Fe	33.4	10.2	15.8
Ni-W	8.3	2.7	4.2

[a] Reaction conditions: pre-reduced temperature (550 °C), reaction temperature (230 °C), catalyst mass (0.05 g), P_{H2} (4.0 MPa), H_2 flow rate (120 mL/min), WHSV (1.3 min⁻¹).

Table S11 Hydrogenation of toluene^[a]

Catalyst (BEA)	X- _{toluene} (%)	Y- methylcyclohexane (%)	Y- _{others} b (%)	r- cycloalkanes ^c	TOF_{Ni}^d	TOF- _M
Ni	15.0	11.2	3.8	35.8	23.5	23.5
Ni-Fe	15.8	10.9	4.8	37.7	24.0	21.4
Ni-Mo	19.0	11.1	7.9	45.3	21.0	18.5
Ni-W	6.7	5.0	1.7	15.7	10.4	9.5

[a] Reaction conditions: 4.0 MPa H₂, 230 °C, (120 mL/min), 0.05 g catalyst, reduction temperature = 550 °C, WHSV =2.2 min⁻¹, and the conversion is an average over the 20-40 min.

[b] Others include cyclohexane, 1,3-dimethylcyclopentane and methylcyclopentane.

[c] Cycloalkanes formation rate per catalyst mass per minute, and the rate is an average over the 20-40 min, unit $(10^{-4} \cdot \text{mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1})$.

[d] TOF_{Ni} is defined as rate for cycloalkanes formation base on the effective moles of surface Ni sites (as shown in Table 1), unit: min⁻¹.

Catalyst (BEA)	X- _{cyclohexanol} (%)	Y- _{cyclohexane} (%)	Y- _{cyclohexene} (%)	L[p]
Ni	12.1	7.8	4.3	247
Ni-Fe	13.8	8.5	5.3	281
Ni-Mo	11.5	5.9	5.6	236
Ni-W	6.3	0.2	6.1	189

Table S12 HDO of cyclohexanol^[a]

[a] Reaction conditions: H_2 pressure (4.0 MPa), reaction temperature (230 °C), H_2 flow rate (120 ml/min), catalyst mass (15 mg), reduction temperature (550 °C), WHSV (20.4 min⁻¹), and the conversion is an average over the 20~30 min.

[b] Cyclohexanol conversion rate per catalyst mass per minute, and the rate is an average over the $20\sim30$ min, unit (10^{-4} ·mol ·min⁻¹·g⁻¹).



Figure S11. XRD patterns of Ni/BEA (a) and Ni-Fe/BEA (b) catalysts with different prereduction temperatures

Cataly	Reducti	Х-	Y-	Y-	Y-	Y-	R-	r-	
st	on	quaiae	cycloboxa	cycloboxo	bonzo	others[cycloboxano/bonzo	cycloboxano	e]
(BEA)	T (°C)	ol	ne (%)	ne	ne	b]	[C] ne	[d]	
		(%)		(%)	(%)	(%)			
Ni	350	7.1	2.1	0.3	0.1	3.9	21	7.8	5.1
Ni	450	7.4	2.2	0.4	0.1	3.8	22	8.2	5.4
Ni-Fe	350	4.8	1.1	0.3	0.04	2.2	27	4.1	2.6
Ni-Fe	450	13.0	4.9	1.1	0.5	5.3	10	18.3	11.6

Table S13. HDO of guaiacol over catalysts with varying reduction temperature^[a]

[a] Reaction conditions: reaction temperature (230 °C), catalyst mass (0.05 g), P_{H2} (4.0 MPa), H₂ flow rate (120 mL/min), WHSV (3.12 min⁻¹), and the conversion is an average over the 20~40 min. [b] Other products include cresol, 1,2-dimethoxybenzene, phenol and toluene.

[c] R-_{cyclohexane/benzene} = Ratio of cyclohexane yield to benzene yield.

[d] Cyclohexane formation rate per catalyst per minute, and the rate is an average over the 20~40 min, unit $(10^{-4} \cdot \text{mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1})$.

[e] TOF_{Ni} is defined as rate for cyclohexane formation base on the effective moles of surface Ni sites (as shown in Table 1), unit: min⁻¹.

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