Supporting information

Solventless hydrodeoxygenation of isoeugenol and dihydroeugenol in the batch and continuous modes over zeolite-supported FeNi catalyst

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1. Experimental

a)

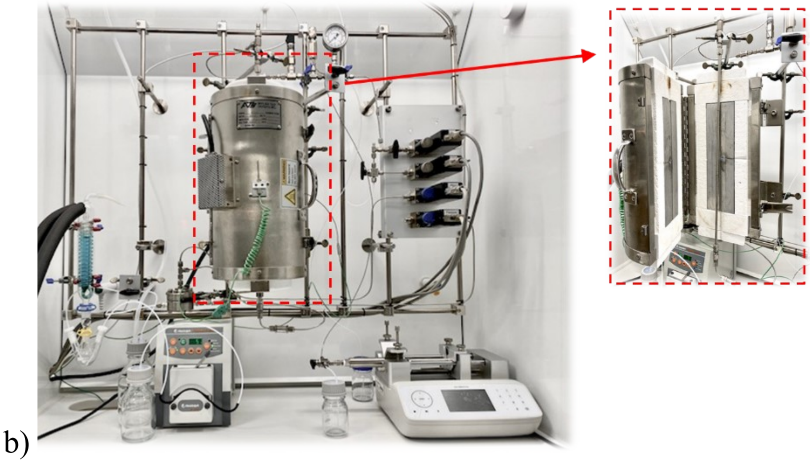


Figure S1. Photos of the experimental setup: a) batch, b) continuous mode.

2. Definitions

The conversion of isoeugenol (X_{IE}) was calculated by:

$$X_{IE} = \frac{n_{IE,0} - n_{IE,t}}{n_{IE,0}} * 100\% \tag{1}$$

where $n_{IE,0}$ is the initial isoeugenol molar concentration and $n_{IE,t}$ is the isoeugenol molar concentration at time t.

The conversion of dihydroeugenol (X_{DHE}) was calculated by:

$$X_{DHE} = \frac{n_{IE,0} - n_{IE,t} - n_{DHE,t}}{n_{IE,0} - n_{IE,t}} * 100\% \tag{2}$$

where $n_{DHE,t}$ is the dihydroeugenol molar concentration at time t.

The mass balance (MB) was calculated by:

$$MB_{(l)} = \frac{c_{(l),t} + c_{(H2O),t}}{c_{(l),0}} * 100\% \tag{3}$$

$$MB_{(g)} = \frac{c_{(g),t}}{c_{(l),0}} * 100\% \tag{4}$$

$$MB_{(ad)} = \frac{c_{(ad)}}{c_{(l),0}} * 100\% \tag{5}$$

$$MB_{total} = MB_{(l)} + MB_{(g)} + MB_{(ad)} \tag{6}$$

where $c_{(l),0}$ is the initial mass concentration of the liquid reactant (time 0), $c_{(l),t}$ is the sum of liquid-phase reactant and products at time t, $c_{(g),t}$ is the sum of gas-phase products at time t, and $c_{(ad)}$ are heavy compounds adsorbed on the catalyst (coke) defined by $c_{(ad)}=m_{coke,TGA}/(Q_{v,reactant}\cdot t)$ [g/L].

The liquid phase carbon balance closure ($CB_{(l)}$) was calculated by:

$$CB_{(l)} = \frac{\sum n_{i,t} \cdot CN_i}{n_0 \cdot CN_{reactant}} * 100\% \tag{7}$$

where $n_{i,t}$ is molar concentration of i compound at time t, and CN is the carbon number.

Yield and selectivity of products (Y_i, S_i) were calculated by:

$$Y_i = \frac{n_{i,t}}{n_0} * 100\% \tag{8}$$

$$Y_{total} = \frac{\sum n_{i,t}}{n_0} * 100\% \tag{9}$$

$$S_i = \frac{Y_{i,t}}{\sum Y_{i,t}} * 100\% \tag{10}$$

The reaction rates (r) and turnover frequency (TOF) are calculated as follows [45]:

$$r_{batch} = \frac{\Delta n}{\Delta t \cdot m_{cat}} \tag{11}$$

$$r_{cont.} = \frac{\Delta \dot{n}}{m_{cat}} \tag{12}$$

$$TOF_{batch} = \frac{\Delta n \cdot V_l}{\Delta t . n_{metals(surface)}} \tag{13}$$

$$TOF_{cont.} = \frac{\Delta \dot{n}}{n_{metals(surface)}} \tag{14}$$

where $\Delta n/\Delta t$ denotes reacted moles (isoeugenol or dihydroeugenol) per time interval Δt (one to 30 min) in a batch reactor, $\Delta \dot{n}$ denotes the change in molar flow rate of the feed at time zero and time t in a continuous reactor, m_{cat} is the catalyst mass, V_l is liquid volume, $n_{metals(surface)} = (n_{(Fe)} \times dispersion_{(Fe)}/100 + n_{(Ni)} \times dispersion_{(Ni)}/100)$ is exposed moles of metals.

The residence time in the continuous reactor (τ) was calculated according to the following equation:

$$\tau = \frac{V_{CB} \cdot \varepsilon}{Q_{v(l)}} \tag{15}$$

where V_{CB} is the catalyst bed volume, ε is porosity of the catalyst bed (0.4) and $Q_{v(l)}$ is the feedstock flowrate.

3. Catalyst characterization results

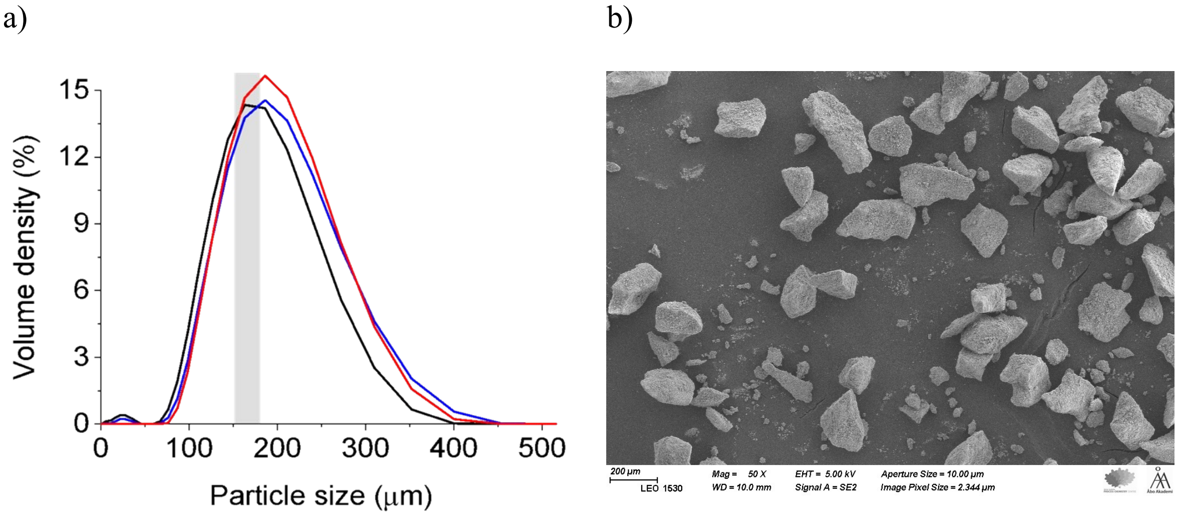


Figure S2. a) particle size distribution of fresh (black) and spent catalysts from the batch experiment (blue, Table 4, entry 1) and the continuous mode experiment (red, Table 4, entry 5) with isoeugenol as a reactant, b) SEM image of fresh catalyst.

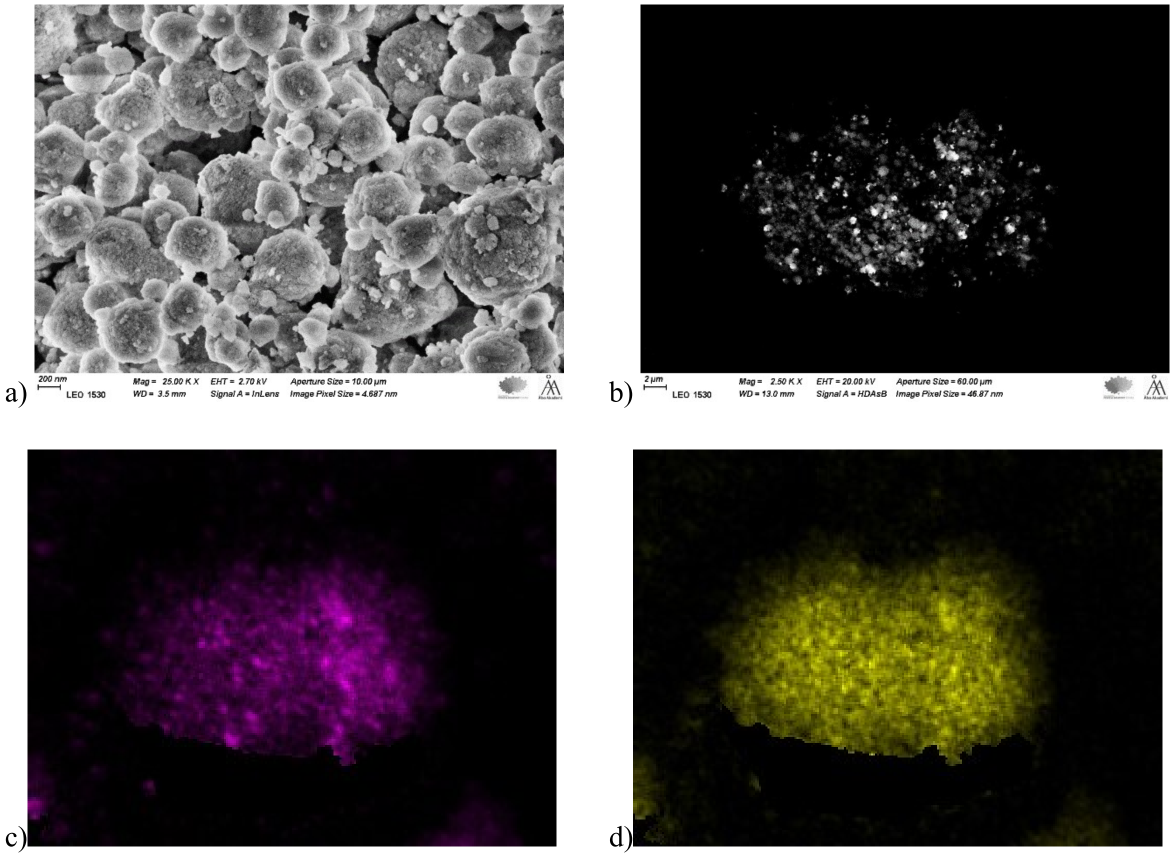
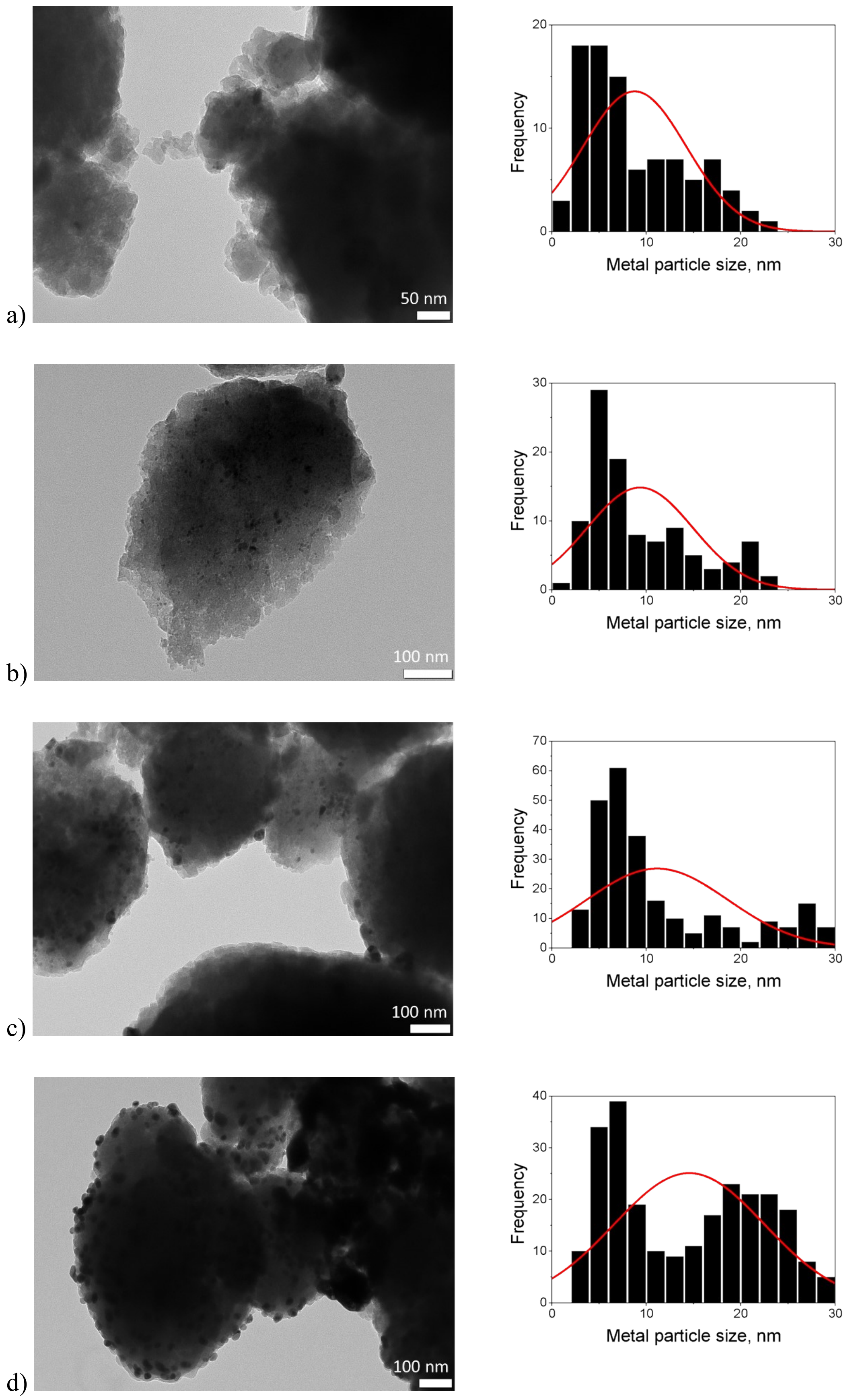


Figure S3. a) scanning electron microscope (SEM) image, b) back-scattered electron (BSE) image, c,d) energy dispersive X-ray (EDX) mapping analysis of Fe (c) and Ni (d).

Table S1. Chemical composition of fresh and spent catalysts. Molar SiO_2/Al_2O_3 and Fe/Ni ratios, mol/mol, and metal concentrations determined by EDX and ICP-OES. Legend: IE – isoeugenol.

Catalyst	EDX				ICP-OES		
	c_{SiO2}/c_{Al2O3}	c_{Fe}/c_{Ni}	c_{Fe}	c_{Ni}	c_{Fe}/c_{Ni}	c_{Fe}	c_{Ni}
	mol/mol	*mol/mol*	*wt%*	*wt%*	*mol/mol*	*wt%*	*wt%*
5-5 wt% Fe-Ni/H-Beta-300	159	1.1	4.6	4.5	1.0	4.5	4.7
spent catalyst, (batch, IE)	-	-	-	-	1.0	3.7	3.9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50 nm
Frequency
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10
20
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10
20
30
Metal particle size, nm
b)
100 nm
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0
10
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30
Metal particle size, nm
c)
100 nm
Frequency
0
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20
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50
60
70
0
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Metal particle size, nm
d)
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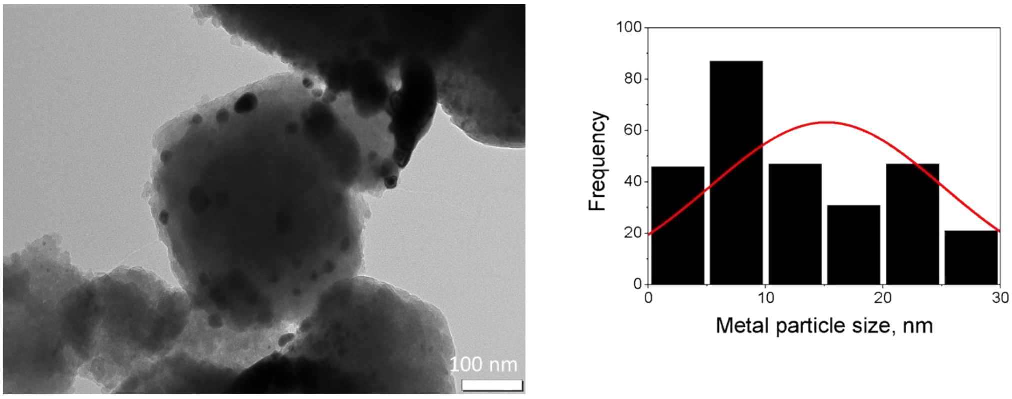
30
Metal particle size, nm


100 nm
Frequency
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40
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80
100
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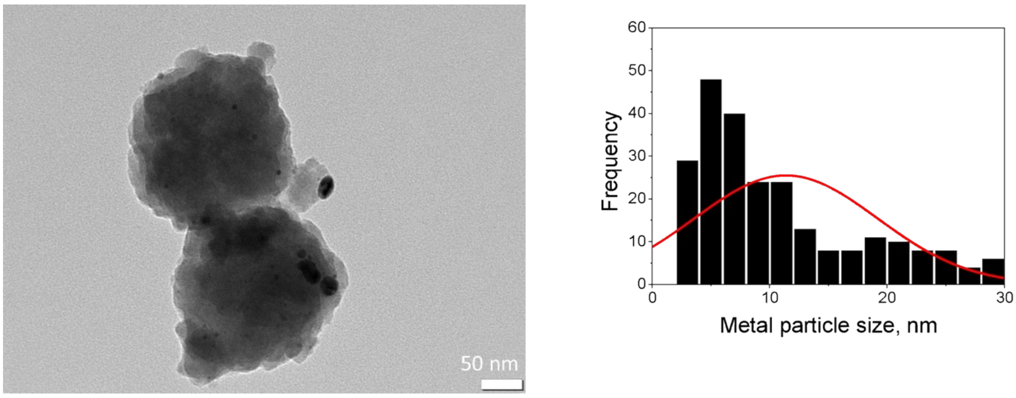
20
30
Metal particle size, nm

e)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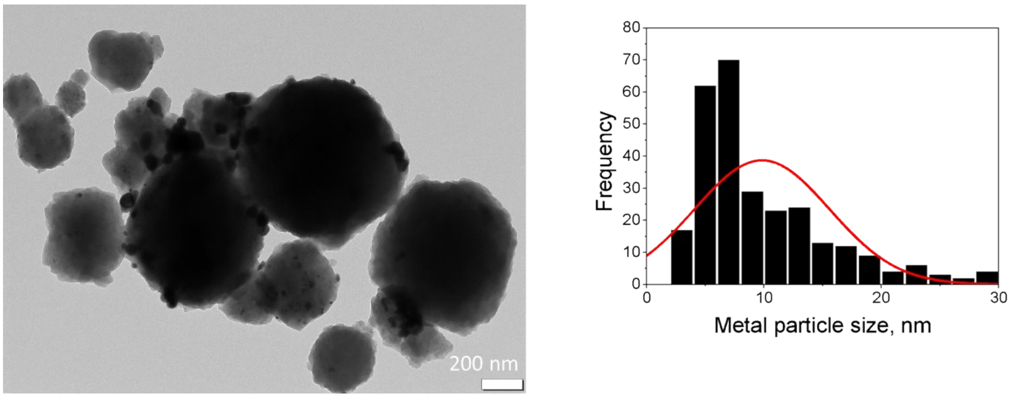
Metal particle size, nm

f)


200 nm
Frequency
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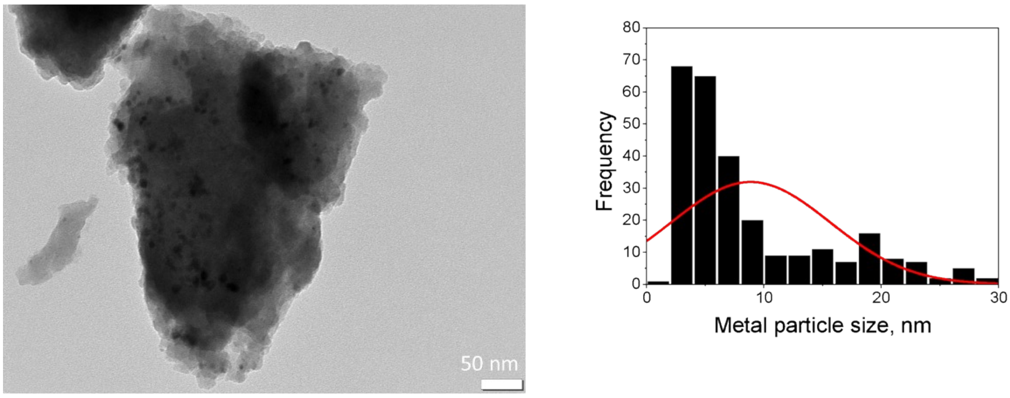
Metal particle size, nm

g)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Frequency
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Metal particle size, nm

h)

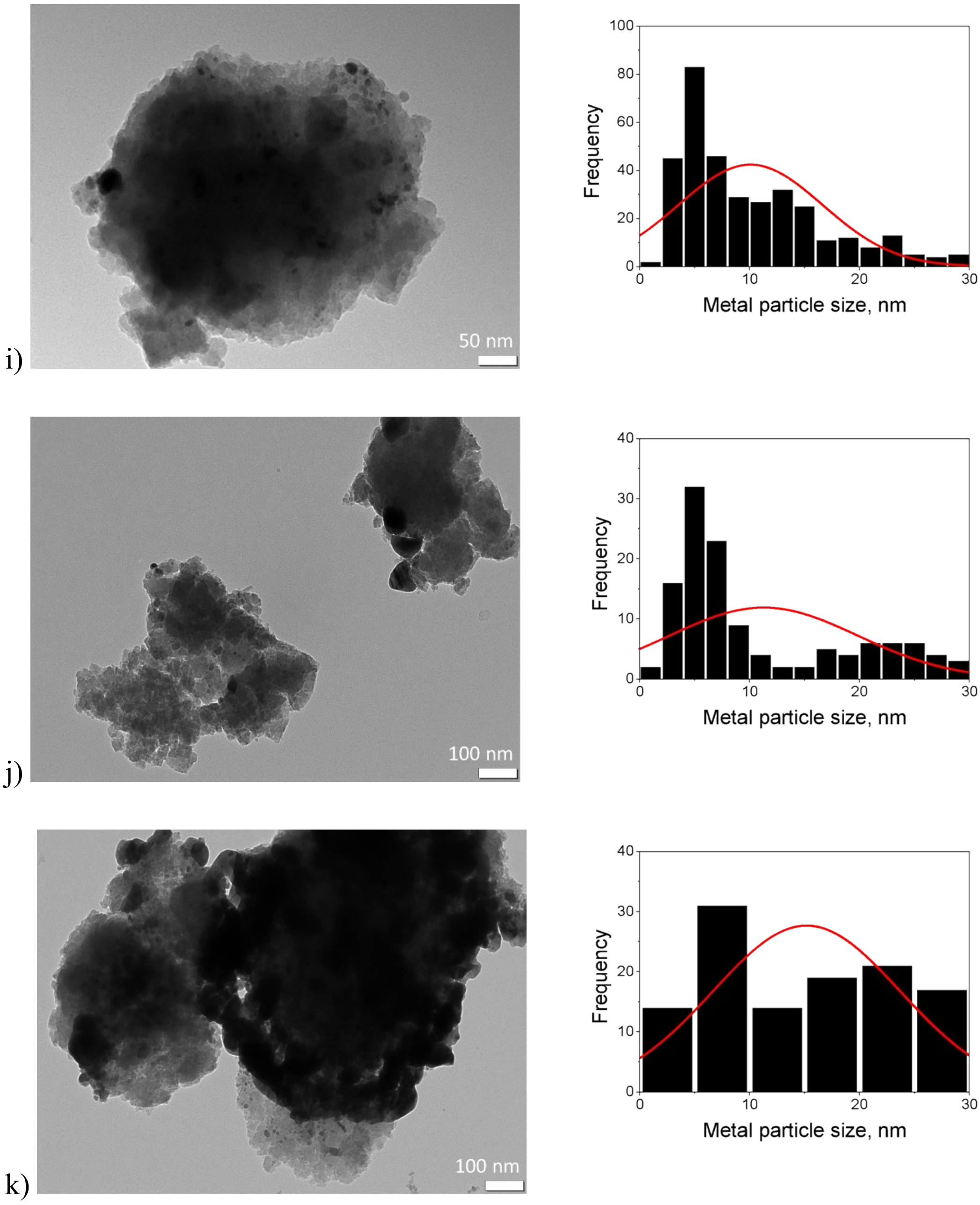
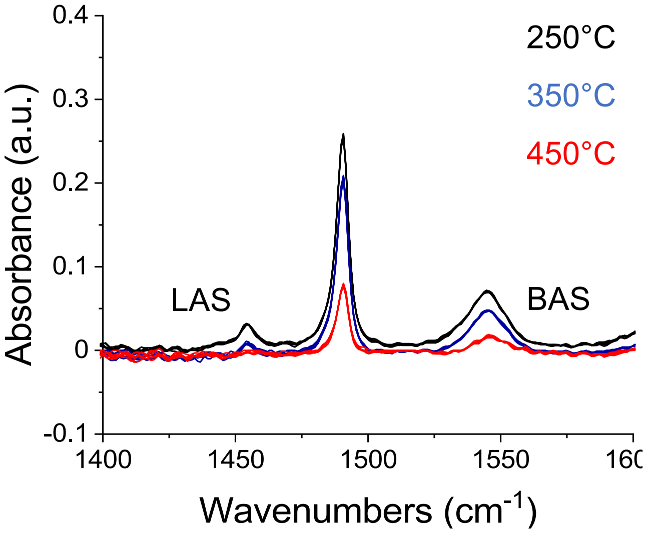
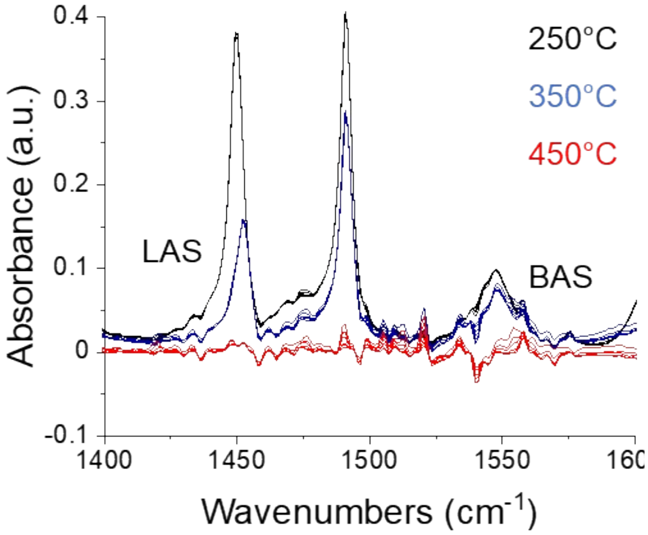


Figure S4. TEM images of fresh and spent catalysts and histogram of FeNi particle size: a) fresh non-reduced, b) fresh reduced, c) spent (Table 1, entry 1), d) spent (Table 1, entry 2), e) spent (Table 1, entry 3), f) spent (Table 1, entry 4), g) spent (Table 1, entry 5), h) spent (Table 1, entry 6), i) spent (Table 1, entry 7), j) spent (Table 1, entry 8), k) spent (Table 1, entry 10).


0.4
0.3
0.2
0.1
0
-0.1
Absorbance (a.u.)
250°C
350°C
450°C
LAS
BAS
1400
1450
1500
1550
160
Wavenumbers (cm^{-1})

a)


0.4
0.3
0.2
0.1
0
-0.1
Absorbance (a.u.)
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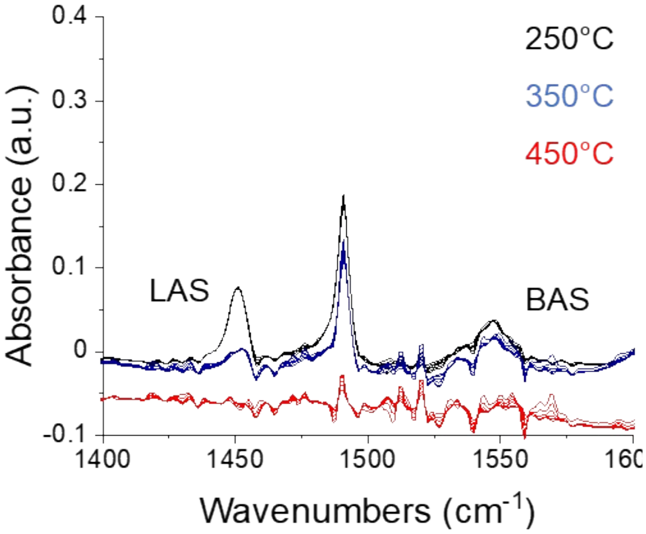
350°C
450°C
LAS
BAS
1400
1450
1500
1550
160
Wavenumbers (cm^{-1})

b)

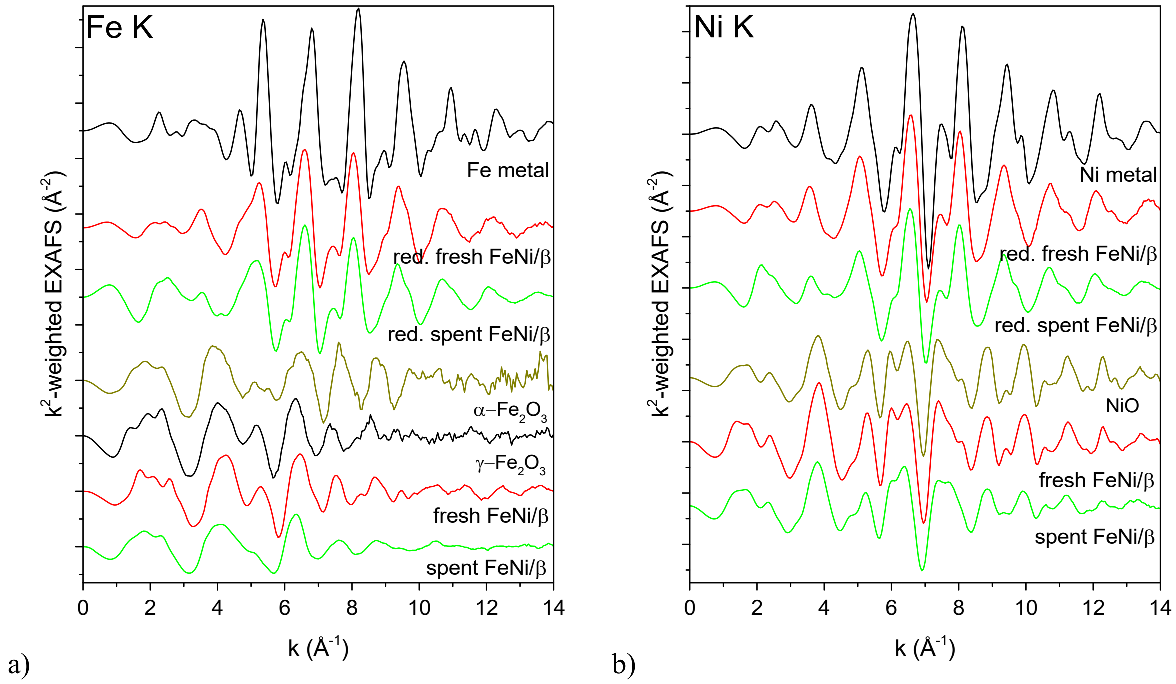

0.4
0.3
0.2
0.1
0
-0.1
Absorbance (a.u.)
250°C
350°C
450°C
LAS
BAS
1400
1450
1500
1550
160
Wavenumbers (cm^{-1})

c)

Figure S5. FTIR-pyridine spectra: a) H-Beta-300, b) 5-5 wt% Fe-Ni/H-Beta-300, c) spent catalyst (batch, IE). Legend: BAS – Brønsted acid sites, LAS – Lewis acid sites. Description: using pyridine (>99%, Acros Organics) as a probe molecule, Fourier transform infrared spectroscopy (FTIR, ATI Mattson) was used for qualitative and quantitative determination of both Brønsted and Lewis acid sites. A catalyst (10-20 mg) was shaped into a thin self-supporting pellet with a radius of 0.65 cm and placed inside the FTIR cell. Pretreatment was performed at 450°C under vacuum. The temperature was decreased to 100°C after 1 h, and two background spectra were recorded. The probe molecule (pyridine) was absorbed for 30 minutes at 100°C before being desorbed by evacuation at various temperatures. Three desorption temperatures were designated: 250°C accounting for weak, medium, and strong sites, 350°C reflecting medium, and strong sites, and 450°C is related to the strong acid sites. The spectra were collected six times for each temperature ramp. The spectral bands at 1545 cm-1 and 1450 cm-1 were used to detect the Brønsted and Lewis acid sites, respectively, during scanning under vacuum at 100°C. The average of six measurements obtained for each temperature and the molar extinction parameters reported by Emeis[1] were used to quantify the acid site.

Table S2. Summary of Fe and Ni first shell coordination environments determined from the analysis of EXAFS spectra of reduced catalysts and reference metal foils (5 μm thick). Note that due to similar X-ray atomic form factors of Fe and Ni these two elements are almost indistinguishable during EXAFS analysis, e.g. fully replacing Ni with Fe does not significally change the fit statistics but decreases coordination number (CN) of the respective shell by approx. 10%. Legend: r – interatomic distances, M – metal, CN – coordination number, σ^2 – mean square deviation of interatomic distances, δE^0 – energy shift, ρ – the absolute misfit between theory and experiment.

Sample	**Edge**	**r (M-O)**	**CN (O)**	**r (M-M)**	**CN (M = Fe and/or Ni)**	**σ^2**	**δE_0**	**ρ**
				Å		*10^{-3} $Å^2$*	*eV*	*%*
Fe metal	Fe K	-	-	2.461(0.006)	8	4.8(0.7)	4.9(1.2)	0.8
				2.845(0.006)	6	4.8(0.7)		
Ni metal	Ni K	-	-	2.491(0.002)	12	6.9(0.3)	6.2(0.3)	0.1
FeNi/H-Beta-300	Fe K	-	-	2.489(0.007)	10.8(1.5)	6.8(1.1)	6.4(1.1)	1.6
	Ni K	-	-	2.491(0.002)	11.2(0.5)	6.9(0.4)	5.1(0.4)	0.1
spent FeNi/H-Beta-300 (batch, IE)	Fe K	1.4(0.3)	1.87(0.02)	2.508(0.005)	9.5(0.8)	7.3(0.7)	7.3(0.8)	0.6
	Ni K	1.5(0.4)	2.02(0.02)	2.496(0.004)	9.1(0.6)	7.4(0.5)	5.1(0.6)	0.2



a) b)

Figure S6. Background extracted k^2-weighted EXAFS spectra in k-space of calcined and reduced FeNi/H-Beta-300 catalyst, also after reaction and exposure to air, and subsequent reduction, as well as relevant reference compounds measured at a) Fe K and b) Ni K edges.

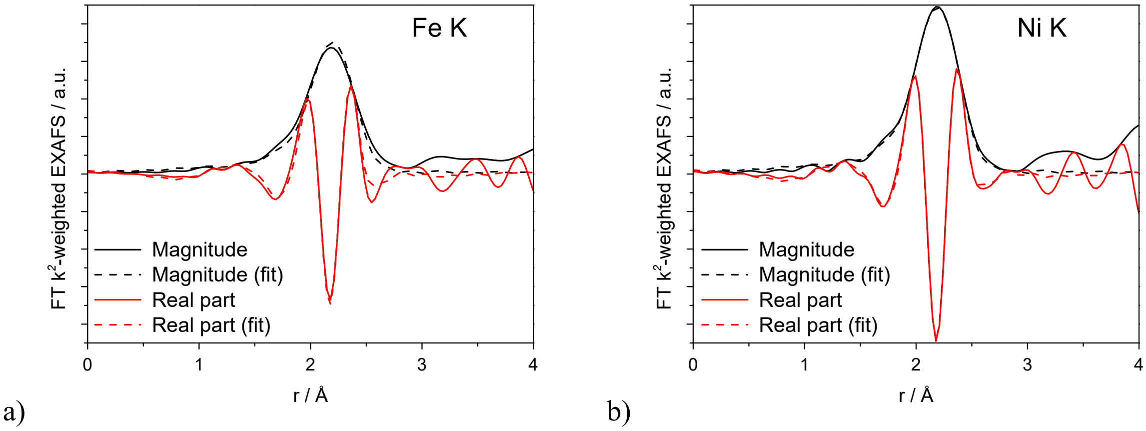


Figure S7. First shell fits of the Fe K and Ni K edge FT EXAFS spectra of reduced FeNi/H-Beta-300 catalyst.

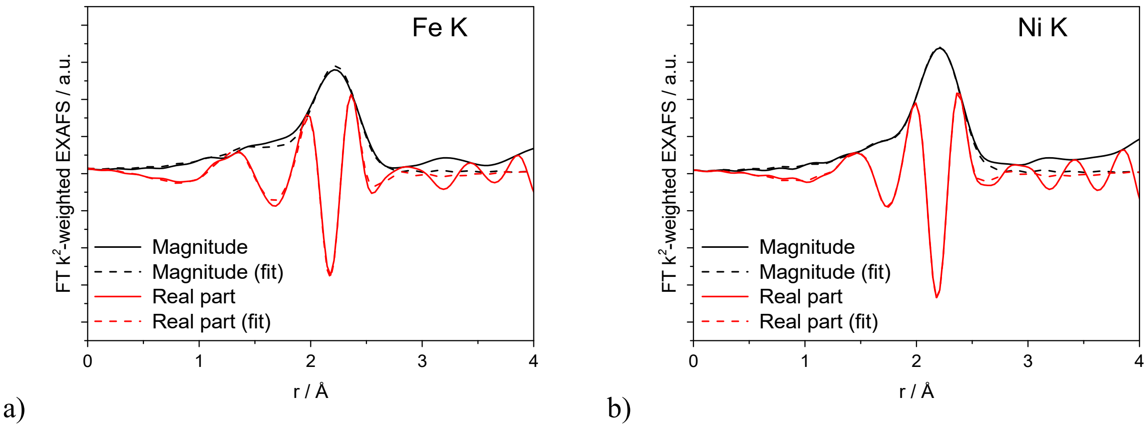


Figure S8. First shell fits of the Fe K and Ni K edge FT EXAFS spectra of spent (exposed to air and reduced again for measurements) FeNi/H-Beta-300 catalyst.

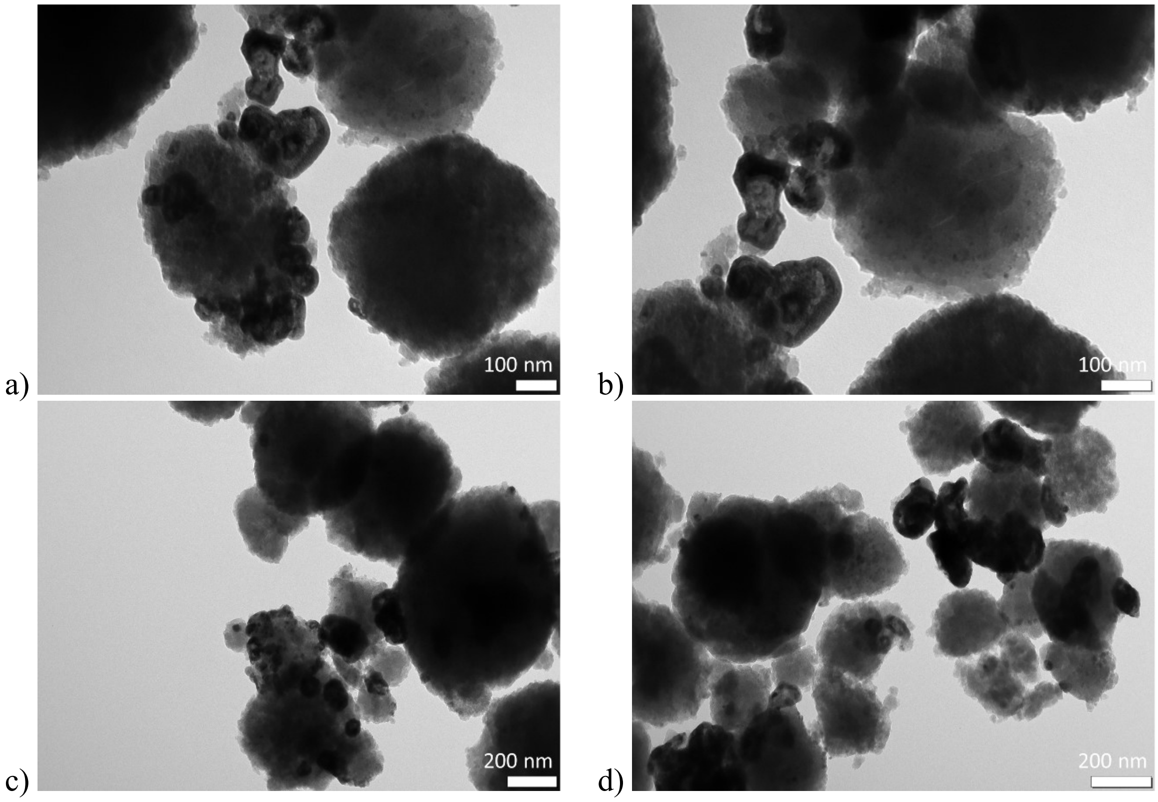


Figure S9. TEM images of regenerated FeNi-H-Beta-300 catalysts, a,b) regenerated at 400 °C and c, d) 900 °C.

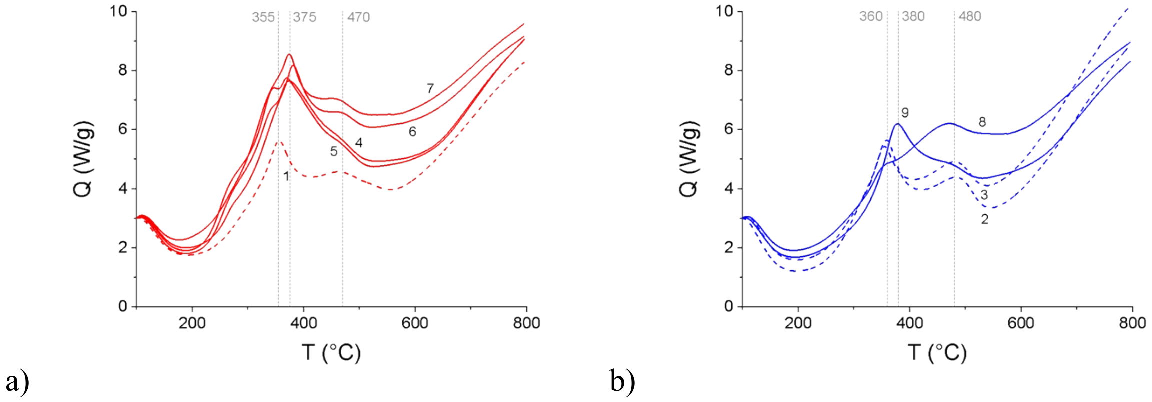


Figure S10. Heat flow as a function of temperature during TGA of spent catalysts: a) from isoeugenol hydrodeoxygenation, b) from dihydroeugenol hydrodeoxygenation. Legend: batch experiment (dash-dash line), continuous experiment (solid line). Notation is the same as in the Table 4.

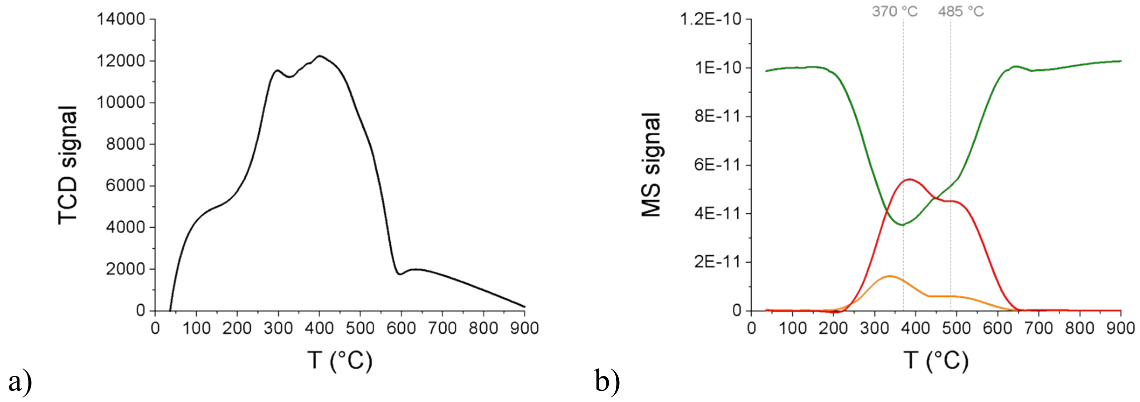


Figure S11. O2-TPO profile: a) TCD signal, b) MS signal of O_2 (green), CO (orange), CO_2 (red). Conditions: to 900 °C with a 5 °C/min ramp under 1.5 ml/min of oxygen and 28.5 ml/min of argon (5 vol% O_2 and 95 vol% Ar).

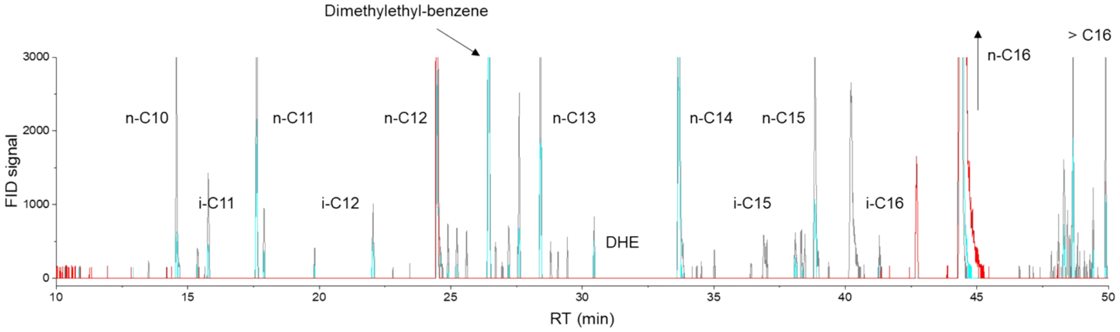


Figure S12. GC-MS analysis of the extracted soluble coke species from the spent catalyst after experiment in the batch reactor: with isoeugenol (grey, Table 4, entry 1), with dihydroeugenol (blue, Table 4, entry 2), with dihydroeugenol with injection of reactant on the preheated reduced catalyst (red, Table 4, entry 3).

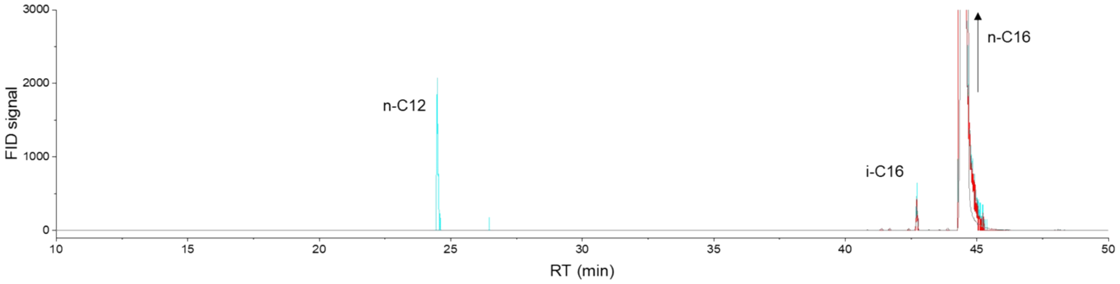


Figure S13. GC-MS analysis of the extracted soluble coke species from the spent catalyst after experiment in the continuous reactor: with isoeugenol (grey, Table 4, entry 5), with dihydroeugenol (blue, Table 4, entry 8), (red, Table 4, entry 9).

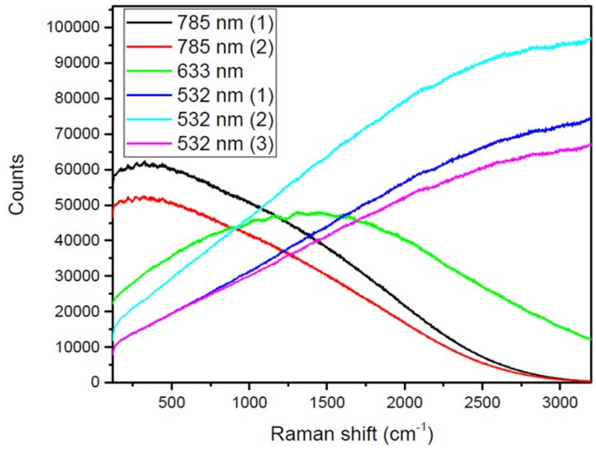
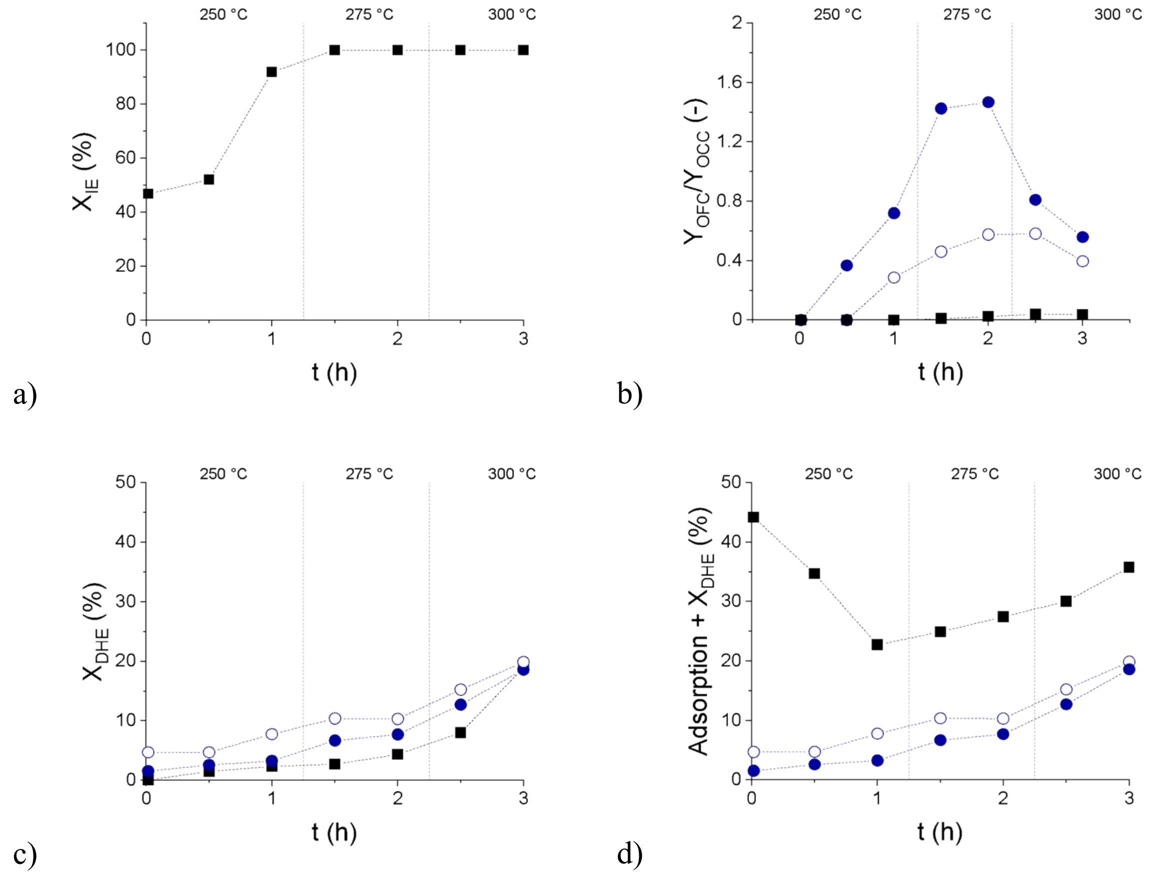
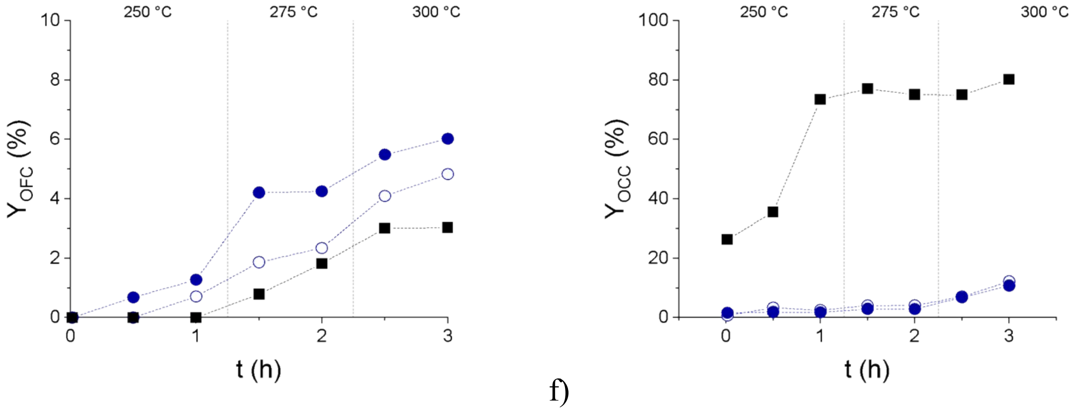


Figure S14. Raman spectra of the spent catalyst used in isoeugenol hydrodeoxygenation in the batch reactor (Table 4, entry 1): laser power 0.05% powder sample on stainless steel plate (black, 785 nm (1)), laser power 0.05% powder sample pressed onto glass plate (red, 785 nm (2)), laser power 0.1% powder sample on stainless steel plate (green, 633 nm), laser power 0.05% powder sample pressed onto glass plate (dark blue, 532 nm (1)), laser power 0.05% sample pressed as a hard pellet (light blue, 532 nm (2)), laser power 0.1% powder sample on stainless steel plate (pink, 532 nm (3)).

4. Catalytic results

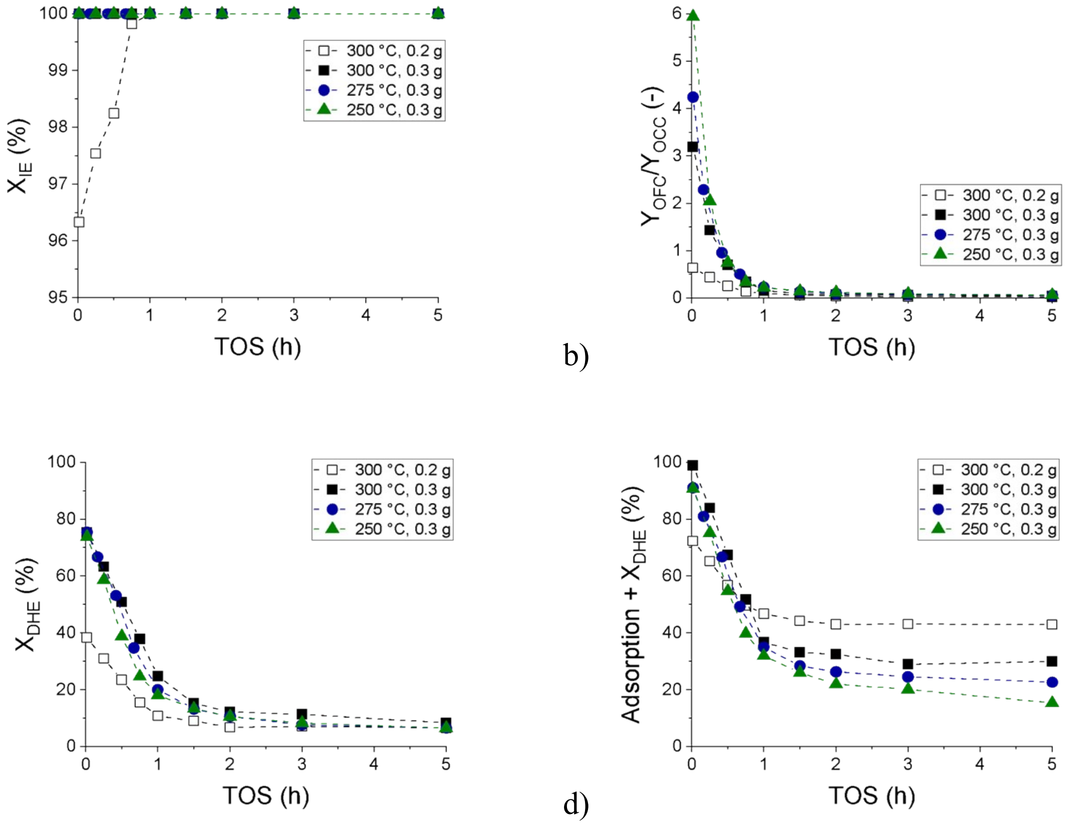




e)

f)

Figure S15. Catalytic results from the batch experiments performed at 250-300 °C, 30 bar with 2.2 g of catalyst in 3 h: a) isoeugenol conversion, b) yield ratio of the oxygen-free to oxygen-containing compounds, c) dihydroeugenol conversion, d) dihydroeugenol conversion with adsorption, e) yield of oxygen-free compounds, f) yield of oxygen-containing compounds. Legend: isoeugenol hydrodeoxygenation without injection (black square), dihydroeugenol hydrodeoxygenation without injection (fulfilled blue circle), dihydroeugenol hydrodeoxygenation with injection (open blue circle).



a)

b)

c)

d)

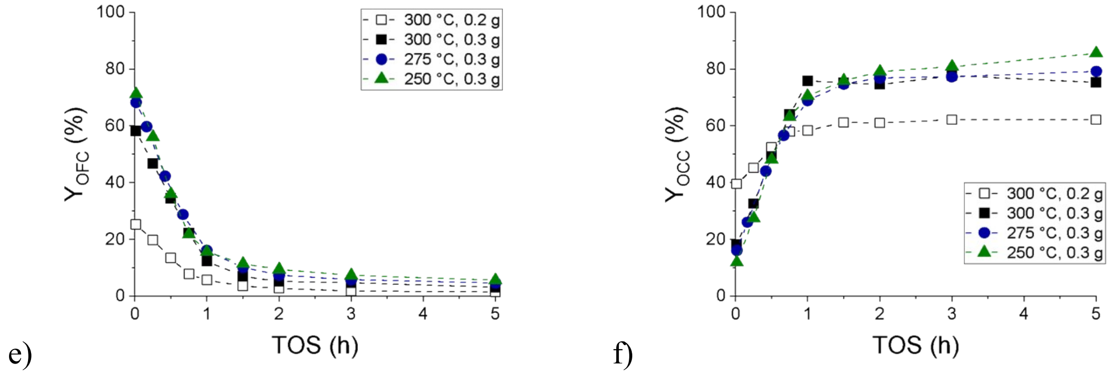


Figure S16. Catalytic results of isoeugenol hydrodeoxygenation from the continuous experiments performed at 250-300 °C, 30 bar with 0.2-0.3 g of catalyst in 5 h of time-on-stream (TOS): a) isoeugenol conversion, b) yield ratio of the oxygen-free to oxygen-containing compounds, c) dihydroeugenol conversion, d) dihydroeugenol conversion with adsorption, e) yield of oxygen-free compounds, f) yield of oxygen-containing compounds.

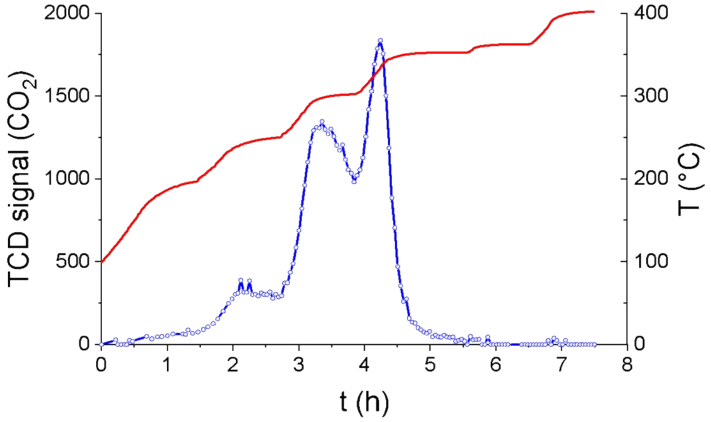


Figure S17. TCD signal of CO_2 (blue line) and temperature profile (red line) during the in-situ catalyst regeneration.

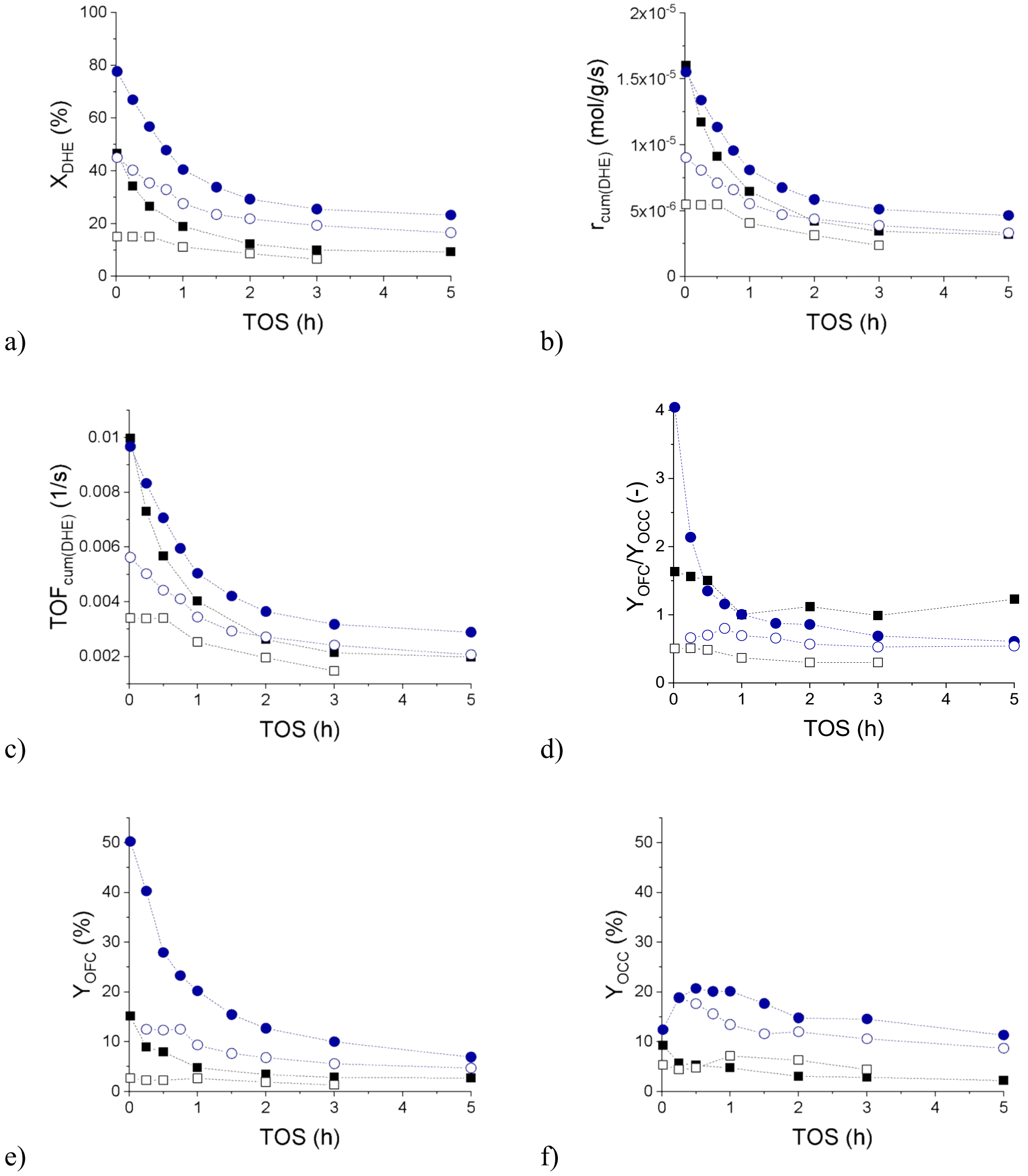


Figure S18. Catalytic results of dihydroeugenol hydrodeoxygenation from the continuous experiments performed at 250-300 °C, 30 bar with 0.2-0.3 g of catalyst in 5 h of time-on-stream (TOS): a) dihydroeugenol conversion, b) cumulative reaction rate, c) cumulative turnover frequency, d) yield ratio of the oxygen-free to oxygen-containing compounds, e) yield of oxygen-free compounds, f) yield of oxygen-containing compounds. Legend: first run (fulfilled black square, Table 6, entry 8a), second run (open black square, Table 6, entry 8b), first run (fulfilled blue circle, Table 6, entry 9a), second run (open blue circle, Table 6, entry 9b).

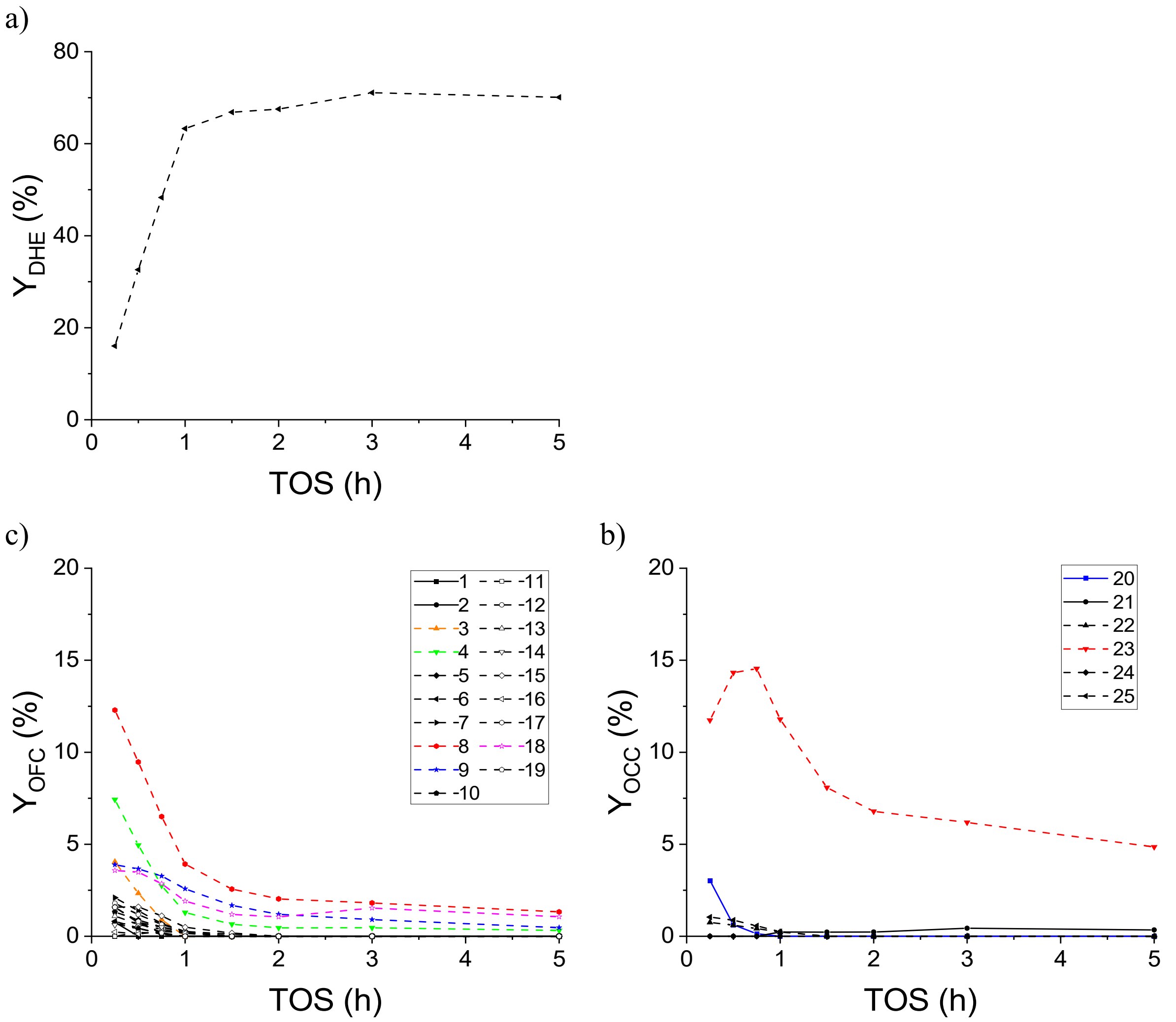


Figure S19. Catalytic results of isoeugenol hydrodeoxygenation from the continuous experiments (Table 6, entry 5) performed at 300 °C, 30 bar with 0.3 g of catalyst in 5 h of time-on-stream (TOS): a) yield of dihydroeugenol, b) yield of oxygen-free compounds, c) yield of oxygen-containing compounds as a function time-on-stream. Notation: 1) methylcyclohexane, 2) 1,2-dimethylcyclohexane, 3) 1,3,5-trimethylcyclohexane, 4) butylcyclopentane, 5) 1,2,4,4-tetramethylcyclopentene, 6) 1-methyl-2-propylcyclopentane, 7) 1-ethyl-3-methylcyclohexane, 8) propylcyclohexane, 9) 1-propylcyclohexane, 10) methylethylcyclopentene, 11) 1-ethyl-4-methylcyclohexane, 12) 3-(2-methylpropyl)-cyclopentene, 13) 1-butenylcyclopentane, 14) 1,3-dimethyl-1-cyclohexene, 15) 1-butenylcyclopentane, 16) propylidencyclohexane, 17) 1-methyl-2-propyl- cyclohexane, 18) propylybenzene, 19) 1-methyl-3-propyl-benzene, 20) 2-ethoxy-2-cyclohexen-1-one, 21) 3-n-propylcyclohexanone, 22) 1-methoxy-4-propyl-benzene, 23) 4-propyl-phenol, 24) 1-methoxy-4-[1-(methyl-d)-benzene, 25) 1,2-dimethoxy-4-n-propylbenzene.

a) b)

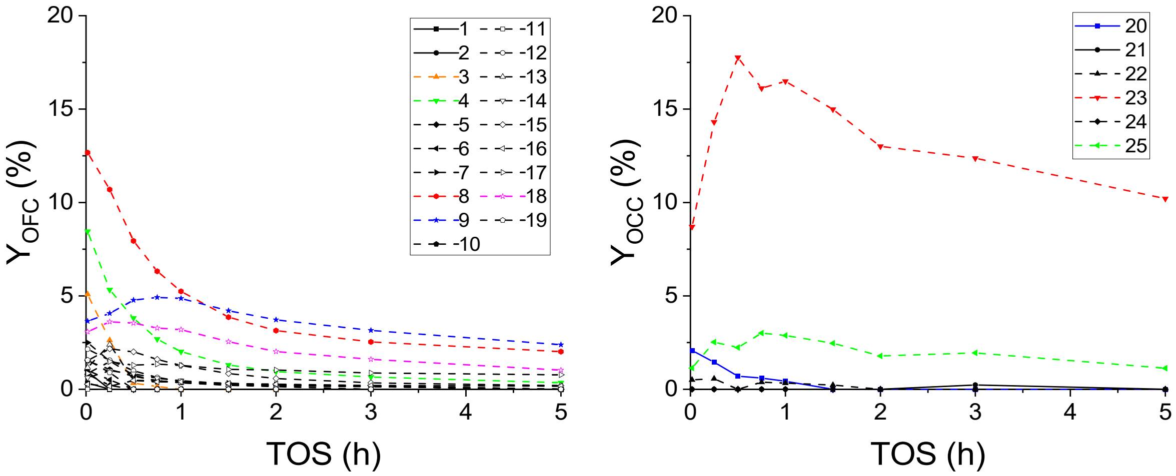
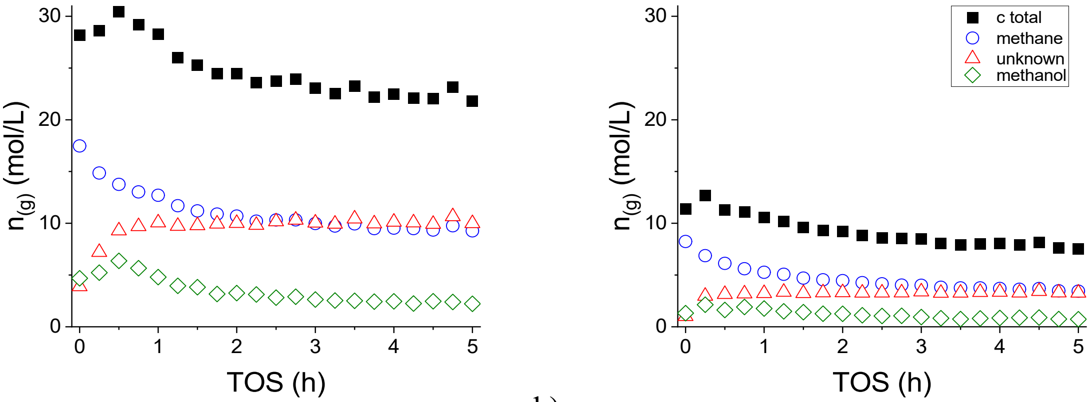


Figure S20. Catalytic results of dihydroeugenol hydrodeoxygenation from the continuous experiments (Table 6, entry 9a) performed at 300 °C, 30 bar with 0.3 g of catalyst in 5 h of time-on-stream (TOS): a) yield of oxygen-free compounds, b) yield of oxygen-containing compounds as a function time-on-stream. Notation: 1) methylcyclohexane, 2) 1,2-dimethylcyclohexane, 3) 1,3,5-trimethylcyclohexane, 4) butylcyclopentane, 5) 1,2,4,4-tetramethylcyclopentene, 6) 1-methyl-2-propylcyclopentane, 7) 1-ethyl-3-methylcyclohexane, 8) propylcyclohexane, 9) 1-propylcyclohexane, 10) methylethylcyclopentene, 11) 1-ethyl-4-methylcyclohexane, 12) 3-(2-methylpropyl)-cyclopentene, 13) 1-butenylcyclopentane, 14) 1,3-dimethyl-1-cyclohexene, 15) 1-butenylcyclopentane, 16) propylidencyclohexane, 17) 1-methyl-2-propyl- cyclohexane, 18) propylybenzene, 19) 1-methyl-3-propyl-benzene, 20) 2-ethoxy-2-cyclohexen-1-one, 21) 3-n-propylcyclohexanone, 22) 1-methoxy-4-propyl-benzene, 23) 4-propyl-phenol, 24) 1-methoxy-4-[1-(methyl-d)-benzene, 25) 1,2-dimethoxy-4-n-propylbenzene.



a) b)

Figure S21. Gas phase analysis of a) isoeugenol (Table 6, entry 5), and b) dihydroeugenol hydrodeoxygenation (Table 6, entry 9a) from the continuous experiments performed at 300 °C, 30 bar with 0.3 g of catalyst in 5 h of time-on-stream (TOS). Legend: total molar concentration of the gas phase (fulfilled black square), methane (blue circle), unknown product 1 (red triangle), methanol (green diamond).

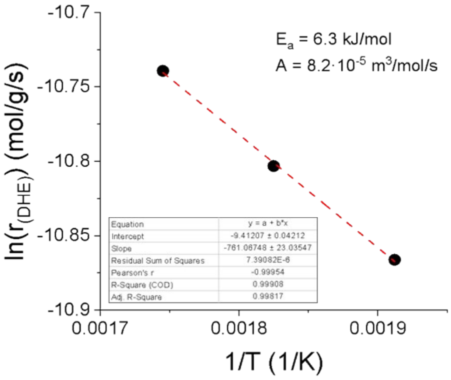


Figure S22. The Arrhenius plot. Conditions: solventless isoeugenol hydrodeoxygenation over 0.3 g of FeNi/H-Beta-300 (150-180 μm) catalyst at 250-300 °C, 30 bar of H_2 with 0.04 mL/min of liquid flow and a 15-fold excess of hydrogen.

References

1. Emeis C.A., Determination of Integrated Molar Extinction Coefficients for Infrared-Adsorption Bands of Pyridine Adsorbed on Solid Acid Catalysts, *J. Catal.*, **1993**, *141*, 347-354. DOI: 10.1006/jcat.1993.1145