

Hydrodeoxygenation of phenolic compounds and lignin bio-oil surrogate mixture over Ni/BEA zeolite catalyst and investigation of its deactivation

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Supplementary information (SI)

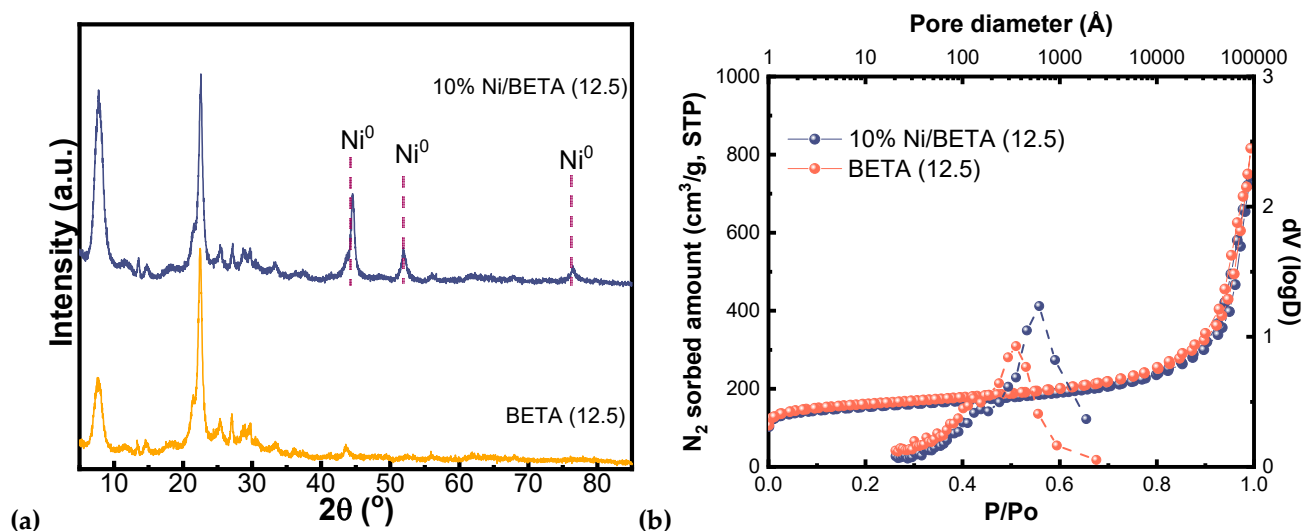


Figure S1: (a) XRD and (b) N₂ physisorption isotherm and BJH pore size distribution of 10%Ni/BETA (12.5) catalysts.

Detailed Analysis of liquid products

The quantification of all the phenolic and aromatic compounds by GC-FID was based on suitable calibration curves of each compound in n-hexadecane. Similarly, the quantification of cyclohexane, methyl-cyclohexane, ethyl-cyclohexane and methyl-cyclopentane products was based on their calibration curves in n-hexadecane. The quantification of the rest cycloalkanes (referred as non-oxygenated compounds) was based on the same response factor with the above cycloalkanes. The GC-FID analysis was performed in the Shimadzu Nexus GC-2030 instrument equipped with a capillary Mega-101 column (30 m × 0.35 mm × 0.45 μm) and flame ionization detector (FID), using air, hydrogen and helium as carrier gas. The temperature program followed for the analysis was: initial temperature of 40 °C was held for 2 min, heating to 100 °C with heating rate 3 °C/min, holding at this temperature for 5 min, heating to 150 °C with heating rate 5 °C/min, holding at this temperature for 5 min and finally heating to 300 °C with heating rate 10 °C/min, holding at this temperature for 5 min. The analysis of the liquid product was directly (without dilution) performed for the hydrodeoxygenation of monomers and after dilution 1:100 in n-hexadecane for the surrogate mixture.

The qualitative analysis was carried out in the gas chromatography-mass spectrometry system (Agilent 6890N-MSD 5973 GC-MS) equipped with an MTX-5 column (Restek, 30 m × 0.25 mm × 0.25 μm). The analysis was performed using 3 μl of the solution, split ratio 1:100, injector temperature 280 °C and using helium as carrier gas, according to the following temperature program: initial temperature of 40 °C was held for 4 min, heating to 300 °C with heating rate 5 °C/min, holding at this temperature for 7 min. The range of the MS detector was m/z=47-500, scanning the whole analysis time except the elution time of solvent. The analysis of the liquid product was directly (without dilution) performed for the hydrodeoxygenation of monomers and after dilution 1:10 in n-hexadecane for the surrogate mixture. The identification of the compounds was based on the NIST0.5 library, assuming similarity above 90%.

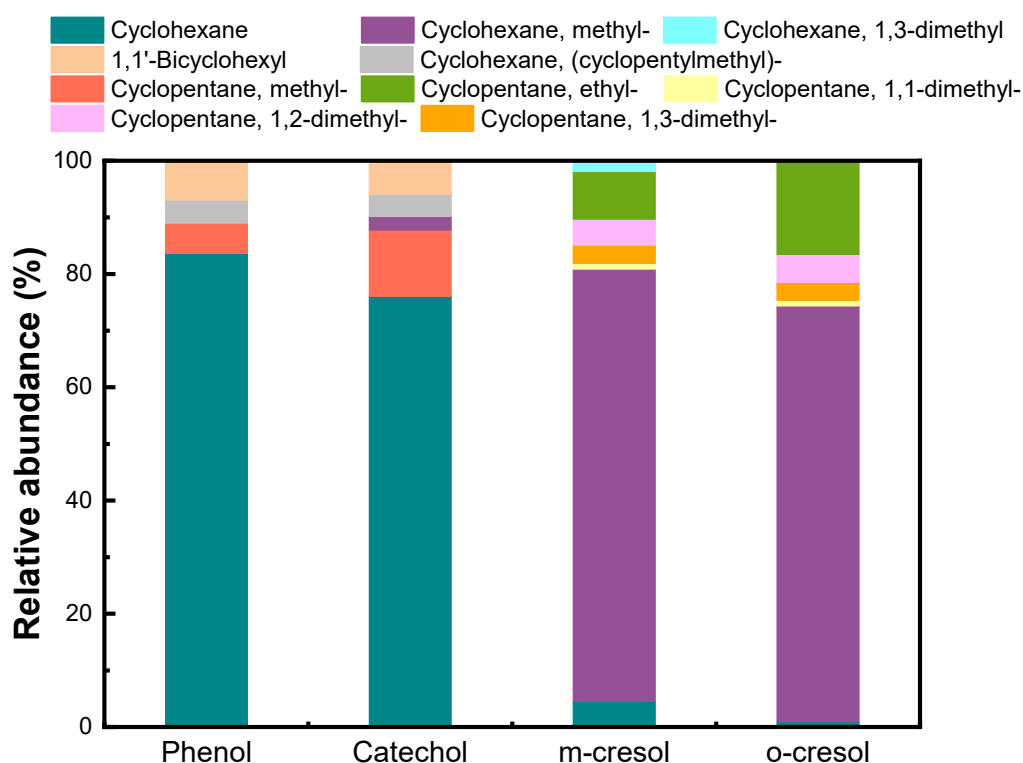


Figure S2: GC-MS analysis of the products obtained after the hydrodeoxygenation of hydroxy and alkyl-substituted phenols at 220 °C, 1 h, 50 bar H₂, 10% Ni/BETA (12.5), C/F=0.2.

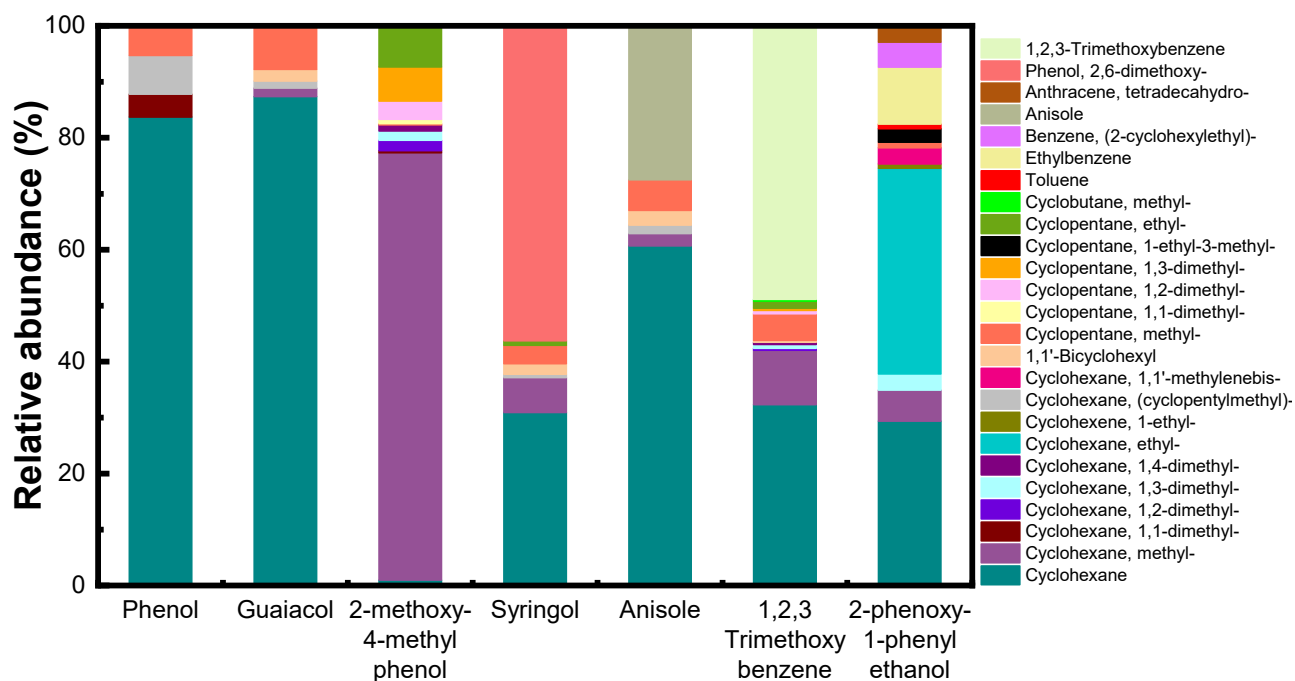
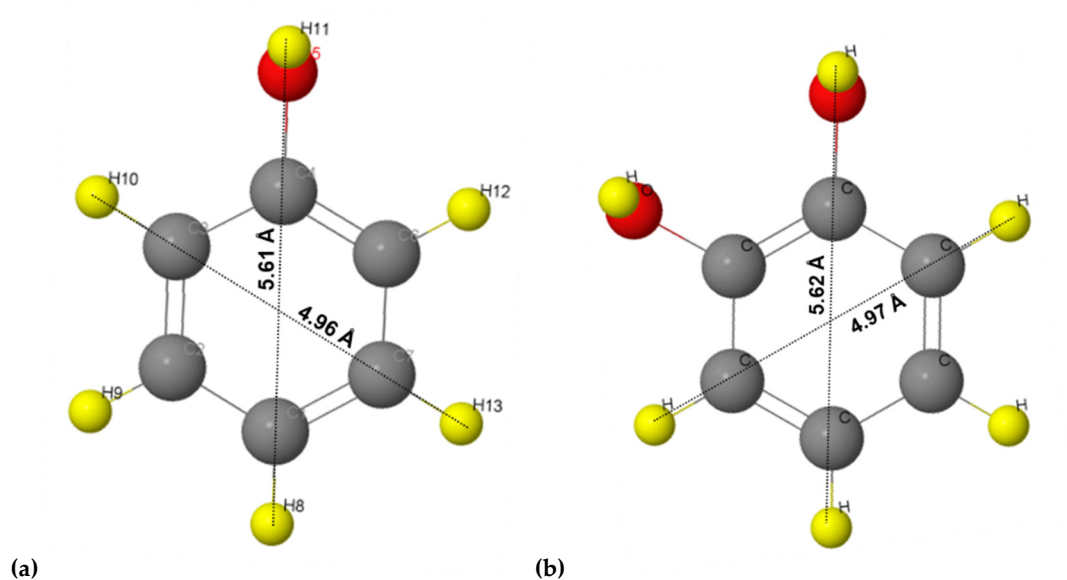
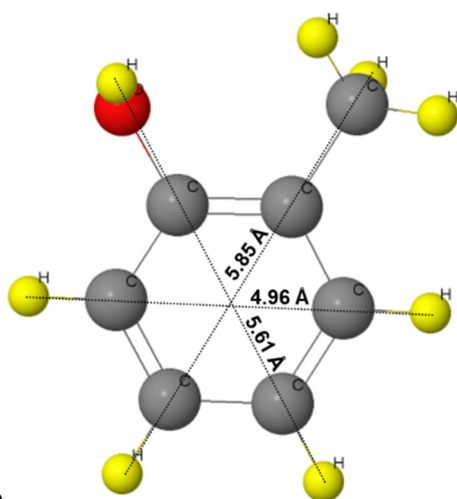
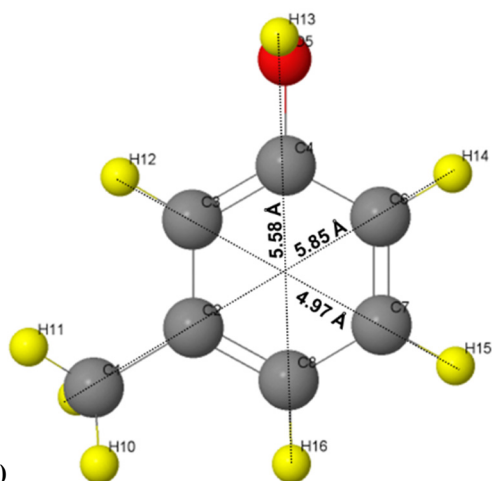


Figure S3: GC-MS analysis of the products obtained after the hydrodeoxygenation of alkoxy-substituted phenols/benzenes at 220 °C, 1 h, 50 bar H₂, 10% Ni/BETA (12.5), C/F=0.2.

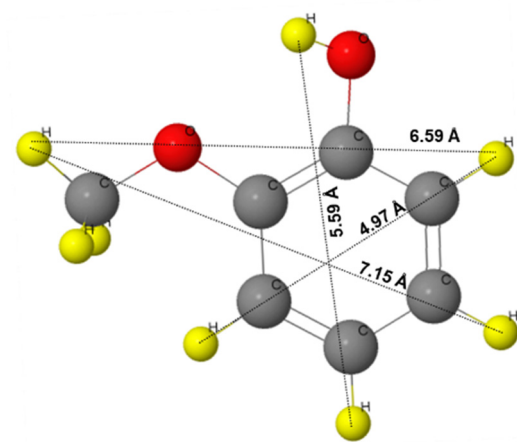




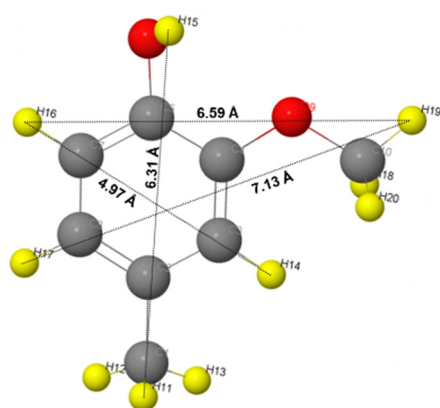
(c)



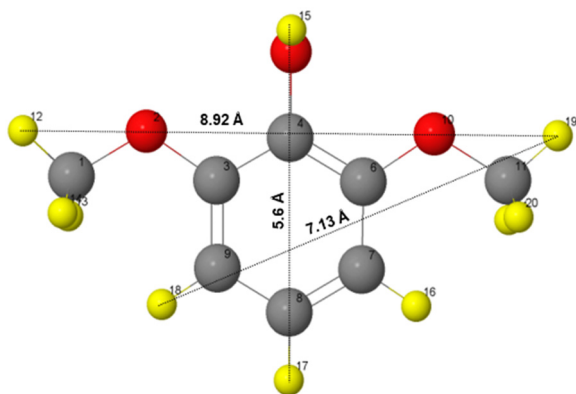
(d)



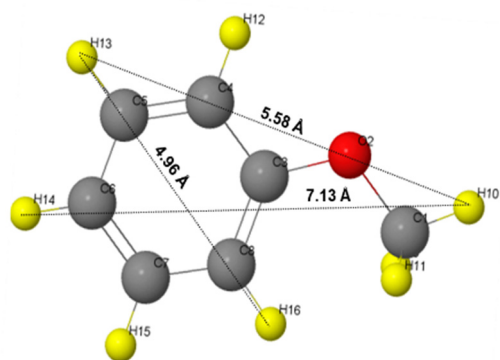
(e)



(f)



(g)



(h)

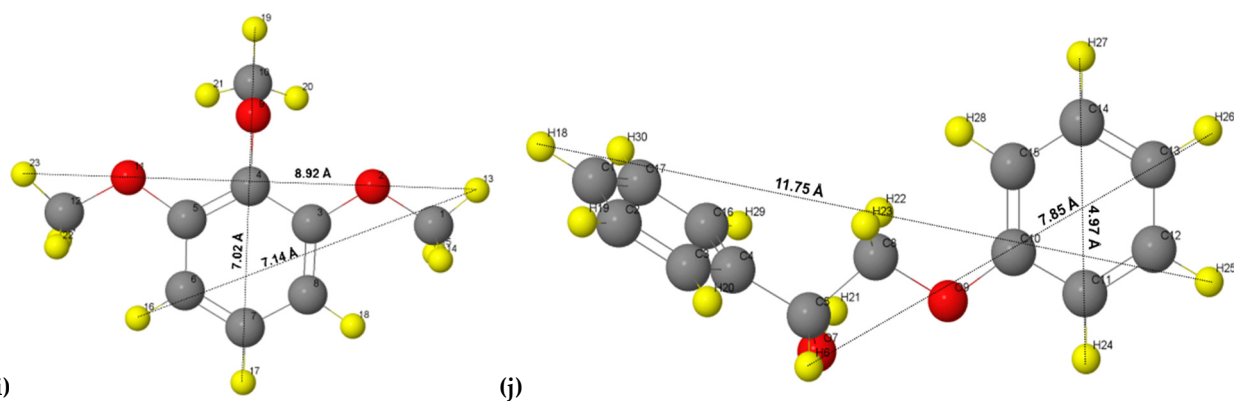


Figure S4: Maximum diameters of: (a) phenol, (b) catechol, (c) o-cresol, (d) m-cresol, (e) guaiacol, (f) 2-methoxy-4-methyl phenol, (g) syringol, (h) anisole, (i) 1,2,3-trimethoxybenzene, (j) 2-phenoxy-1-phenyl ethanol.

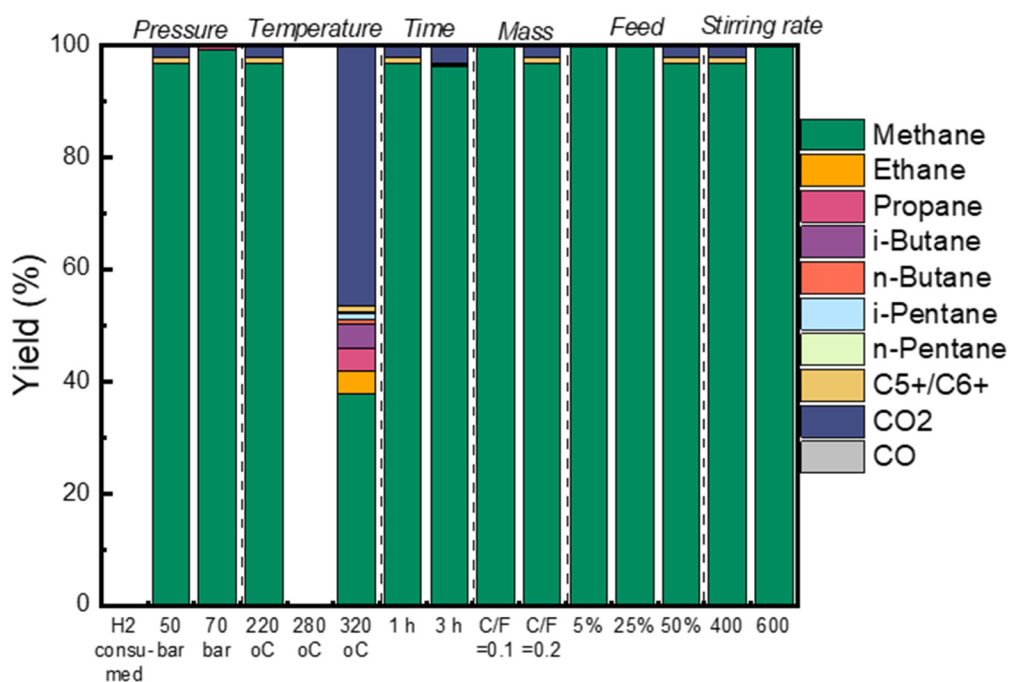


Figure S5: Effect of different reaction conditions on the gaseous products of surrogate mixture hydrodeoxygenation over 10%Ni/BETA (12.5).

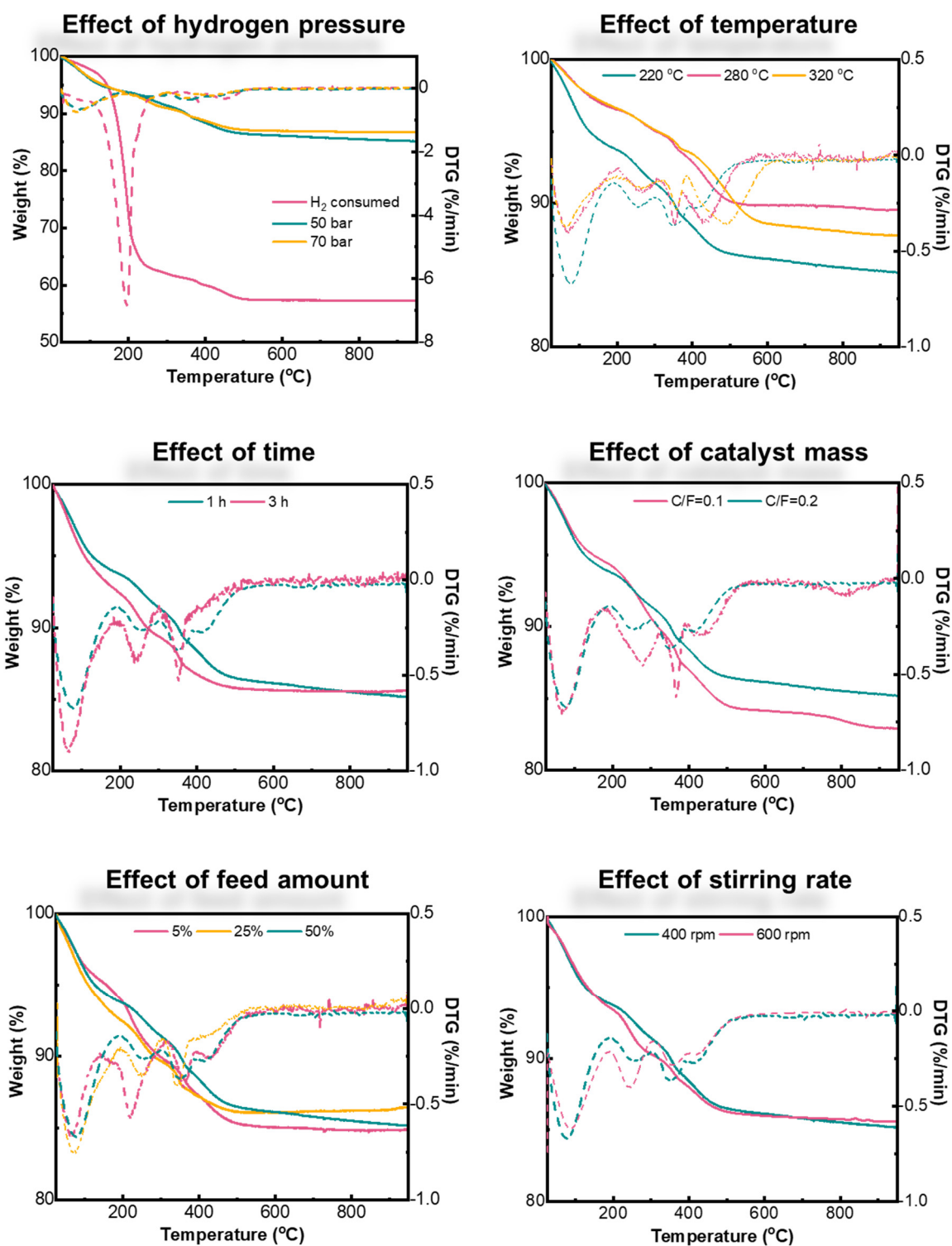


Figure S6: Thermogravimetric analysis of spent 10%Ni/BETA (12.5).

Table S1: Effect of different reaction conditions on the characteristic temperatures and weight losses (TGA) of spent 10%Ni/BETA (12.5).

Catalysts	T _{max} 1, Weight loss, 1	T _{max} 2, Weight loss, 2	T _{max} 3, Weight loss, 3	T _{max} 4, Weight loss, 4
220 °C, 1 h, C/F=0.2, 50%, 400 rpm, H ₂ consumed	-	195 °C, 37.1%	383 °C, 2.9%	452 °C, 2.6%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	78 °C, 6.1%	254 °C, 2.3%	350 °C, 2.8%	409 °C, 2.5%
220 °C, 1 h, 70 bar H ₂ , C/F=0.2, 50%, 400 rpm	70 °C, 6.4%	246 °C, 2.6%	351 °C, 1.8%	419 °C, 2.2%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	78 °C, 6.1%	254 °C, 2.3%	350 °C, 2.8%	409 °C, 2.5%
280 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	71 °C, 3.5%	266 °C, 1.6%	354 °C, 1.4%	428 °C, 3.6%
320 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	66 °C, 3.5%	263 °C, 1.6%	359 °C, 1.4%	487 °C, 5.2%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	78 °C, 6.1%	254 °C, 2.3%	350 °C, 2.8%	409 °C, 2.5%
220 °C, 3 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	63 °C, 7.6%	238 °C, 3.0%	352 °C, 3.7%	-
220 °C, 1 h, 50 bar H ₂ , C/F=0.1, 50%, 400 rpm	67 °C, 5.4%	279 °C, 4.7%	367 °C, 2.6%	433 °C, 3.0%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	78 °C, 6.1%	254 °C, 2.3%	350 °C, 2.8%	409 °C, 2.5%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 5%, 400 rpm	68 °C, 4.7%	222 °C, 5.6%	361 °C, 2.3%	431 °C, 2.3%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 25%, 400 rpm	77 °C, 7.5%	250 °C, 2.9%	340 °C, 3.5%	-
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	78 °C, 6.1%	254 °C, 2.3%	350 °C, 2.8%	409 °C, 2.5%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 400 rpm	78 °C, 6.1%	254 °C, 2.3%	350 °C, 2.8%	409 °C, 2.5%
220 °C, 1 h, 50 bar H ₂ , C/F=0.2, 50%, 600 rpm	87 °C, 6.4%	243 °C, 3.3%	357 °C, 2.2%	418 °C, 2.1%

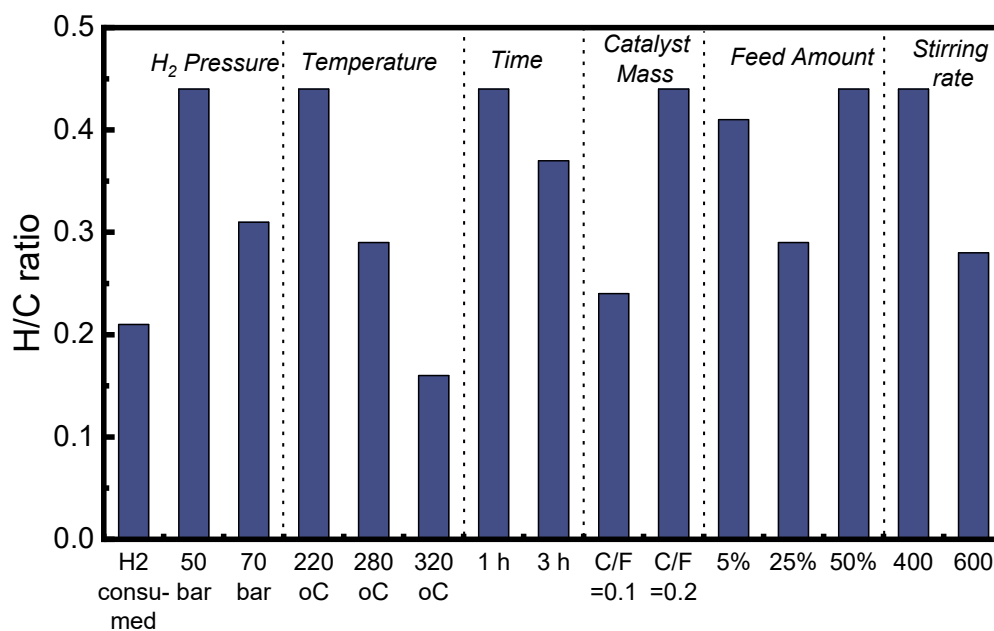


Figure S7: Effect of different reaction conditions on H/C ratio determined via elemental analysis of spent 10%Ni/BETA (12.5).

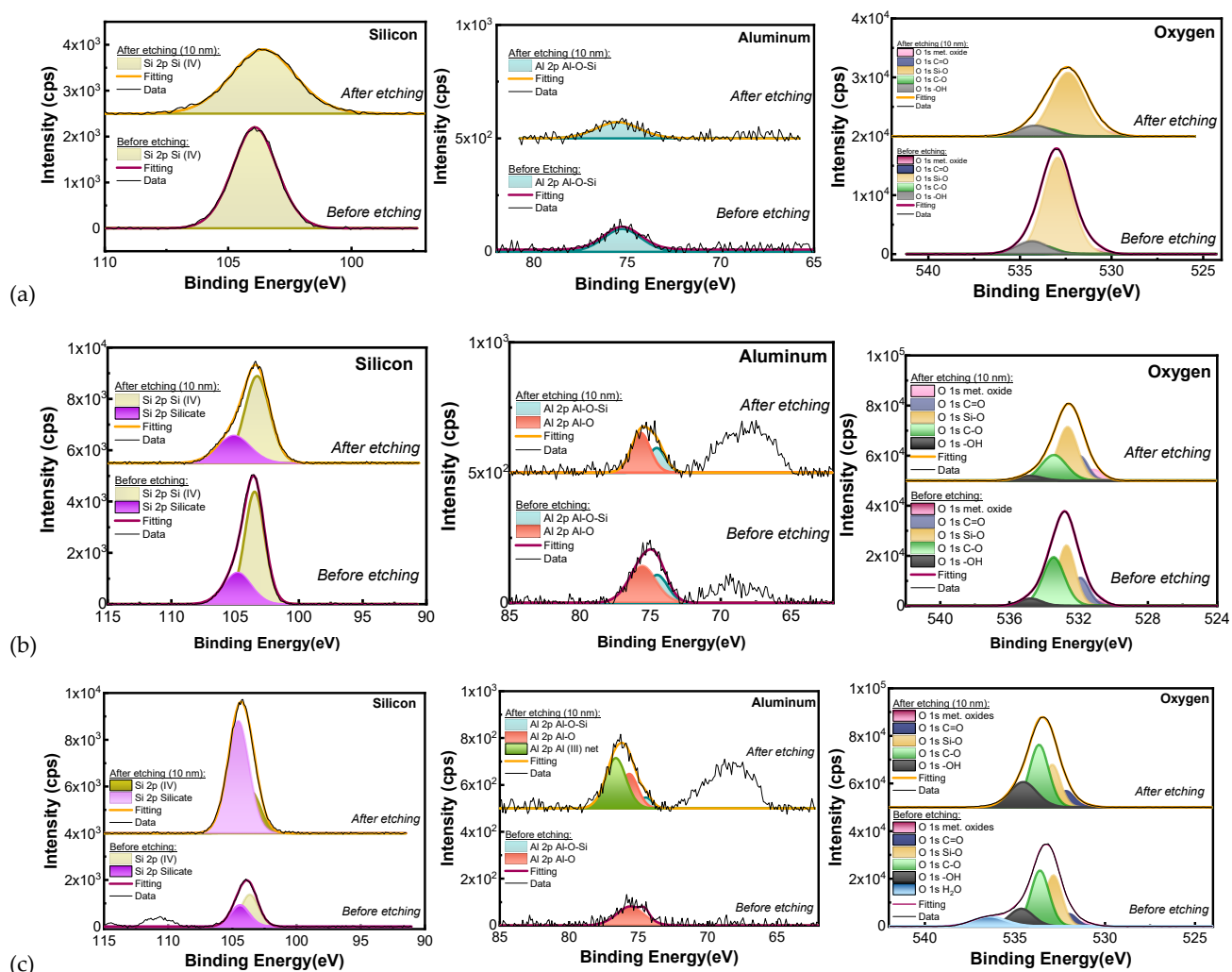


Figure S8: XPS spectra of (a) fresh, (b) used and (c) regenerated catalyst from the experiment 220 °C, 1 h, 50 bar H_2 , C/F=0.2, 50%, 600 rpm. Left: Si 2p, middle: Al 2p and right: O 1s.