Supporting information for:

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1. Experimental details

1.1 Materials

Chemical reactants, calibration standards, and gases were purchased from several commercial suppliers and used as is without further purifications; (5-Hydroxymethylfurfural (>97 wt.%, Carbosynth, reference number FH10853), 5-methylfurfural (99 wt.%, Sigma Aldrich), dimethylfuran (99 wt.%, Sigma Aldrich), 2,5-bis(hydroxymethyl)furan (98 wt.%, VWR), 2,5-bis(hydroxymethyl)tetrahydrofuran (>95 wt.%, Carbosynth), (5-methyl-2-furyl)methanol (98 wt.%, Carbosynth), 1,2,6-hexanetriol (96 wt.%, Sigma Aldrich), 1,5-pentadiol (96 wt.%, Sigma Aldrich), 2-hexanol (99 wt.%, Sigma Aldrich), hydrogen (5.0, Messer), nitrogen (5.0, Messer), NH_3 (5 vol.% in He, Linde), helium (5.0 Messer), carbon monoxide (5 vol.% CO in He, Linde), and tetrahydrofuran (>95 wt.%, Merck Millipore) and 1-butanol (>99%, Merck Millipore) used as solvents. Lanthanum (III) nitrate hexahydrate (99 wt.%, Honeywell Fluka) and nickel (II) nitrate hexahydrate (97 wt.%, Sigma-Aldrich, reference number 72253), and cerium (III) nitrate hexahydrate (99 wt.%, Sigma-Aldrich) were implemented in catalyst preparation using a pure γ-alumina (Spheralite 537, Procatalyse, France) and a commercial mixed γ and α alumina (Merck Millipore) as supports.

1.2 Catalyst preparation

Catalysts were synthesized via incipient wetness impregnation method using aqueous solutions of $Ni(NO_3)_2{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ as precursors dissolved in a specific volume of deionized water equal to the total pore volume of the support. Prior to impregnation, the support was crushed via ball-mill, and sieved to attain the 40 – 100 µm fraction. Succeeding impregnation, catalysts were dried at 110 °C overnight in an oven, then calcined at 400 °C in air for 4 hours. NiCe and NiLa catalysts were impregnated sequentially; ceria or lanthanum was added first, dried, calcined at 400 °C in air then sequentially nickel was added under the same method. Catalyst compositions presented throughout this study denote the weight fraction of the impregnated metal (e. g. 10Ni15Ce refers to 10 wt.% nickel and 15 wt.% ceria). All catalysts are assumed to be supported on Spheralite 537 unless noted otherwise.

1.3 Catalyst activity test for hydrogenation of 5-hydroxymethylfurfural

Catalytic activity tests were carried out in 75mL stainless steel batch reactors (Parr 5000 Series) and mixed with a magnetic stir bar with a stir speed of 1000 rpm. Each reaction consisted of 0.1 g of solid catalyst (pre-reduced weight), 1 g of HMF, and specific amounts of organic solvent (THF or 1-butanol) and Milli-Q water to maintain a constant total volume of 40 mL. Catalysts were reduced in a pure hydrogen flow of 40 mL min^{-1} at 400 °C for 3 hours with a heating rate of 10 K min^{-1} prior to activity tests. Reactions were performed at temperatures in the range of 140 to 200 °C with a heating rate of 5 K min^{-1} and reaction time refers to the length of time only when the desired reaction temperature was reached and does not include the initial heat ramping time. Each autoclave was purged with inert atmosphere (N_2) three times to remove any air in the vessel before being pressurized with 5.0 MPa of H_2 to uphold an approximate H_2:O ratio of 20:1. Immediately after the reaction was completed, the autoclave was rapidly cooled down in water. When the temperature reached below 30 °C, the pressure was released from autoclave before opening to collect the final liquid mixture and spent catalysts.

Auxiliary activity tests that were performed with differing metal oxides (ZnO, CaO, and MgO) each involved 0.1 g of 10Ni15Ce/γ-Al2O3 catalyst in combination with 0.5 g of one of the metal oxides. All three tests were conducted in water-THF mixture and 50 bar of H_2 at 190 °C for 3 hours.

Following the initial activity test, the spent catalysts were used in recyclability tests. Following the first test, catalysts were filtered from the liquid phase and put back in the reactor with a fresh mixture of HMF in solvent (THF with and without water) for the second cycle. After the second cycle, catalysts were instead separated from the liquid phase via centrifugation, washed twice with THF, dried in a nitrogen flow, and then subjected to a reduction pretreatment under the same conditions as previous (400 °C for 3 hours). This was similarly done after the third cycle. After the fourth cycle, the catalysts were additionally calcined in air at 400 °C for 3 hours just prior to the reduction step in the attempt to regenerate the recycled catalyst.

1.4 Liquid Product Analysis

Liquid intermediates and products were first filtered with 0.22µm PET syringe filters before being analyzed off-line by gas chromatography with flame ionization detector (GC-FID) (Nexis GC-2030, Shimadzu). Detected compounds were separated by Zebron ZB-5MS capillary column (60 m × 0.25 mm × 0.25 µm, Phenomenex) and identified with a mass spectrometer and verified with external standards. GC analysis parameters were set with a starting oven temperature of 60 °C and subsequent heat-up to match the injector temperature of 290 °C. Quantification for each product was determined with commercially purchased external standards. The carbon balance for liquid products was consistently above 91% for all activity tests.

1.5 Catalyst Characterization

Surface and textural properties were studied by nitrogen physisorption (ASAP 2020 Micrometrics) to obtain adsorption-desorption isotherms, specific surface area (S_{BET}), average pore diameter (d_p), and pore volume (V_p). Field-emission scanning electron microscopy (FE-SEM) (SUPRA 35 VP, Carl Zeiss) was utilized for observation of morphological properties of catalyst particles. X-ray diffraction (XRD) patterns were characterized using PW3040/60 X'Pert PRO MPD diffractometer at 35 kV and 45 mA with Cu Kα radiation source (λ = 0.154056 nm) in the 2θ range from 10° to 80°, and using JCPDS database for reference. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI-TFA XPS spectrometer produced by Physical Electronics Inc. equipped with X-ray Al-monocromatic source. A low energy electron gun was implemented to avoid sample charging. XPS spectrum O 1s was aligned to the binding energy 531.0 eV, characteristic of Al2O3, too account for possible charging effects. Resulting spectrums were evaluated using Multipak program Version 9.9 which were fitted with Gauss-Lorentz functions and Shirley function was used for background removal.

Hydrogen temperature-programmed reduction (H_2-TPR) was accomplished using a Micrometrics AutoChem II Chemisorption Analyser (Micrometrics, Norcross). 100mg sample of catalyst was placed into a quartz U-tube and pretreated under a 50 mL min^{-1} flow of argon at 300 °C for 30 minutes with a heating rate of 30 K min^{-1} before reduction. Afterwards, the sample was subjected to 40 mL min^{-1} of a 5 vol% H_2 in Ar mixture at a constant heating rate of 10 K min^{-1} up to a maximum of 750 °C. Hydrogen consumption for each catalyst was determined using a TCD detector calibrated using CuO. All temperature programmed desorption (TPD) analysis was performed on same apparatus as TPR. Before TPD measurements, 100 mg catalyst samples were firstly pretreated under the same reduction conditions implemented for catalytic activity tests (400 °C for 3 hours). Samples were subjected to 40 mL min^{-1} of ammonia or carbon dioxide mixtures (10 vol% NH_3 and 5 vol% CO_2 in He) at 60 °C before being purged in He and heated to 600 °C with a constant heating rate of 10 K min^{-1}. Metallic sites were quantified using CO pulse chemisorption in which samples were subjected to 30 pulses of 5 vol% CO in He at -70 °C before being purged in He then heated to 600 °C with a constant heating rate of 10 K min^{-1}. Desorbed compounds were detected using a TCD detector and desired mass spectrums were identified with a GSD 301 T3 Thermostar Mass Spectrometer. Calibration gas mixtures of known concentrations were utilized to estimate metallic, basic, and acid sites. Diffuse reflectance infrared Fourier transform (DRIFT) experiments were obtained with a DiffusIR cell (PIKE Technologies) coupled to Perkin Elmer Frontier spectrometer using pyridine as the probe molecule. 10 mg samples of catalyst was initially pre-treated for 20 minutes in a 100 mL min^{-1} flow of N_2 at 350 °C, cooled to room temperature, then saturated with pyridine vapour in a 50 mL min^{-1} flow of N_2 gas stream for 10 minutes and subsequently evacuated for 10 minutes. The spectra collected are the average of 32 scans with a resolution of 4 cm^{-1} and over 1000–4000 cm^{-1} wave number range.

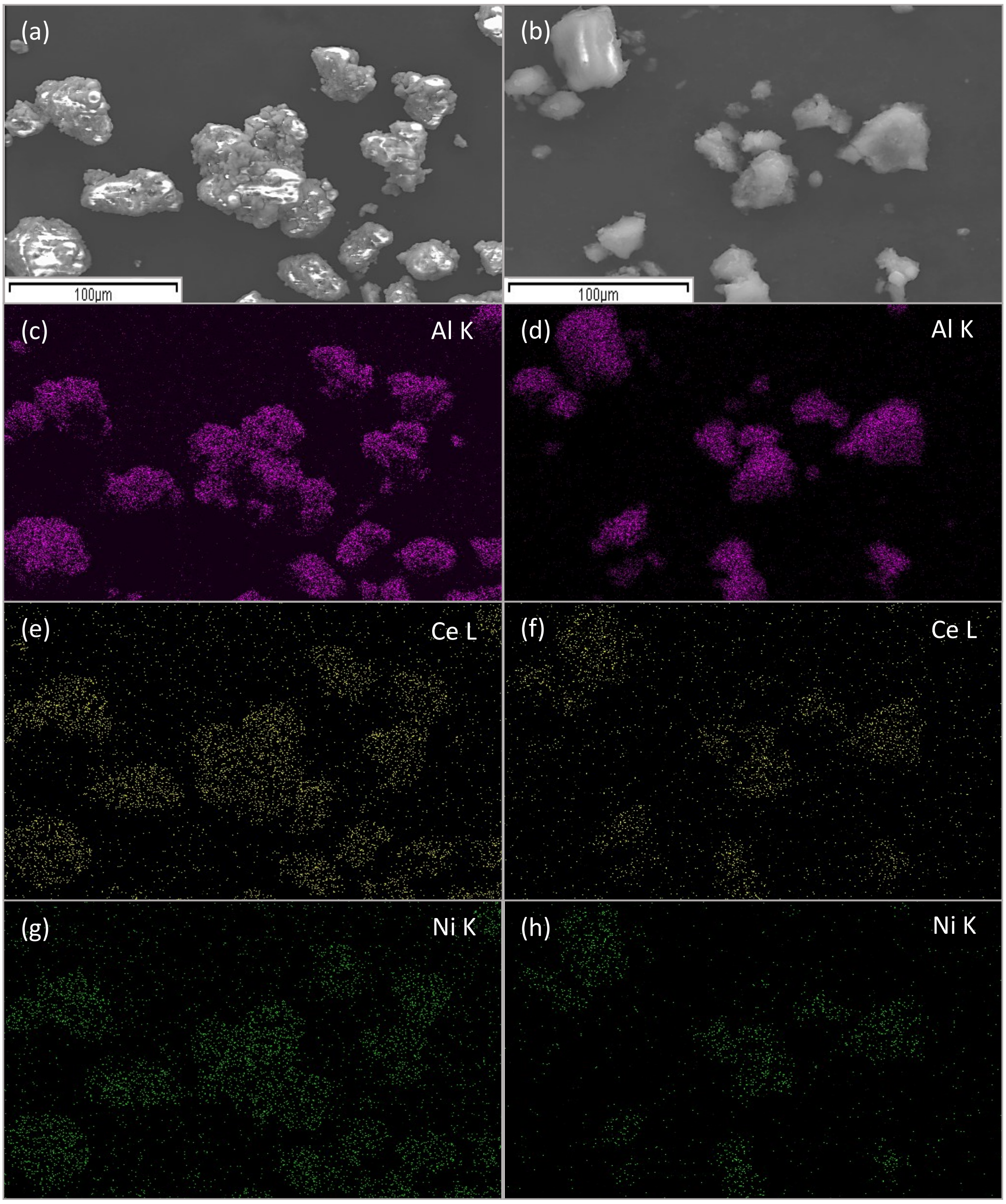


Figure S.1. STEM images (a-b) with corresponding EDXS elemental mappings of reduced (c,e,g) and spent (d,f,h) of 10Ni15Ce catalyst.

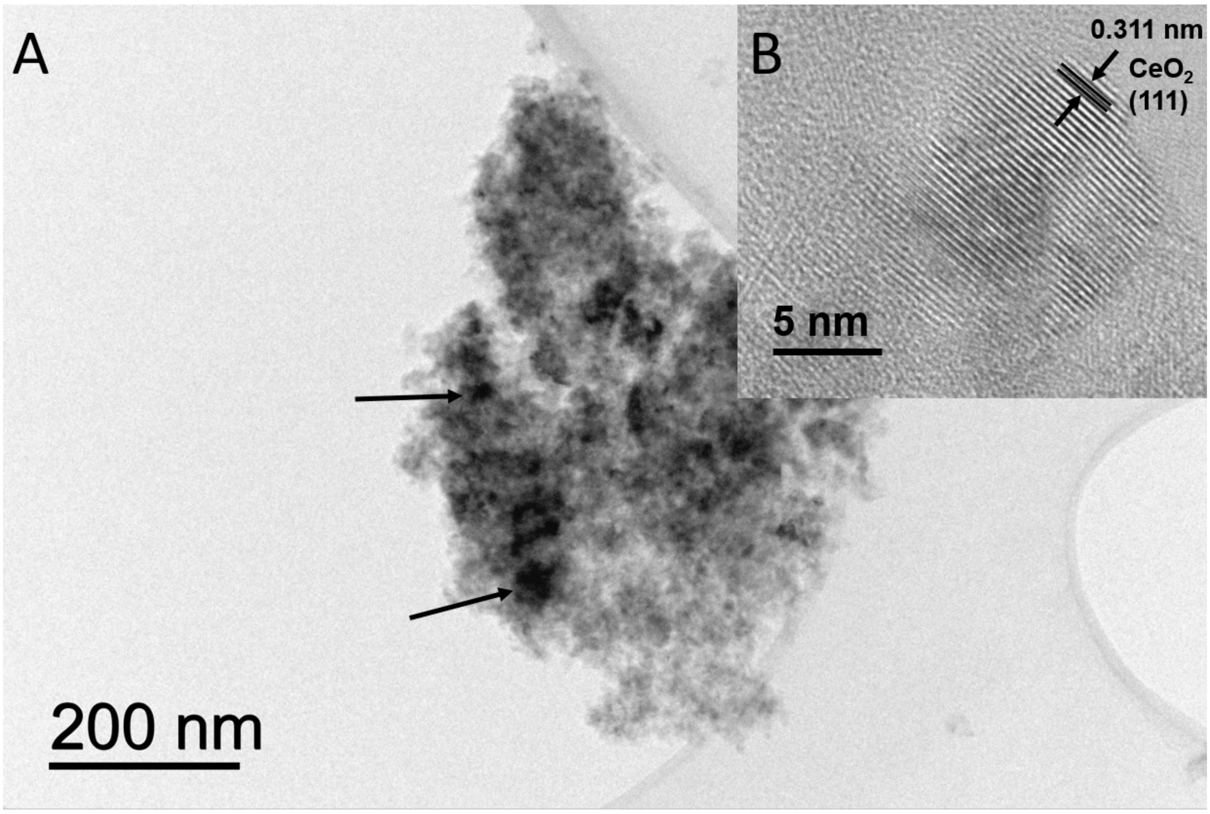


Figure S.2. A) TEM image of 10Ni15Ce catalyst with black arrows pointing to ceria clusters, and B) HR-TEM image of a ceria particle including lattice fringe indicating CeO_2 (111) facet.

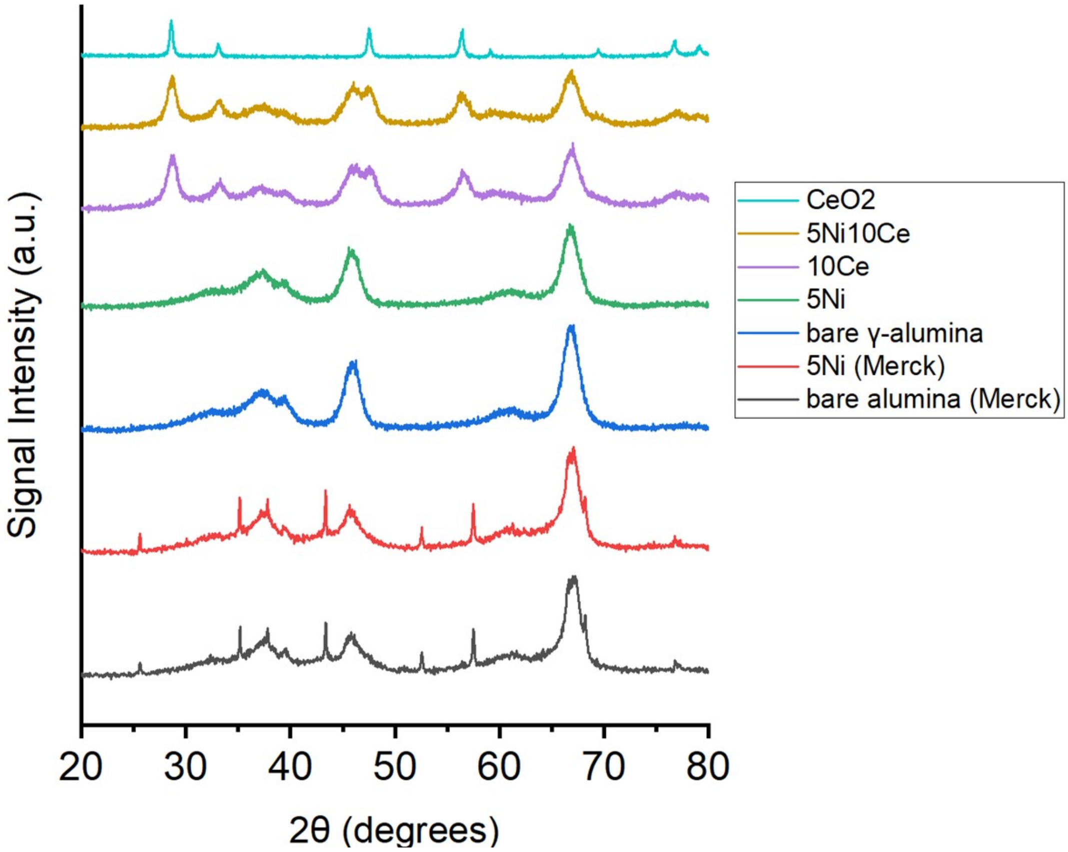


Figure S.3. X-ray diffraction spectra of γ-alumina catalysts

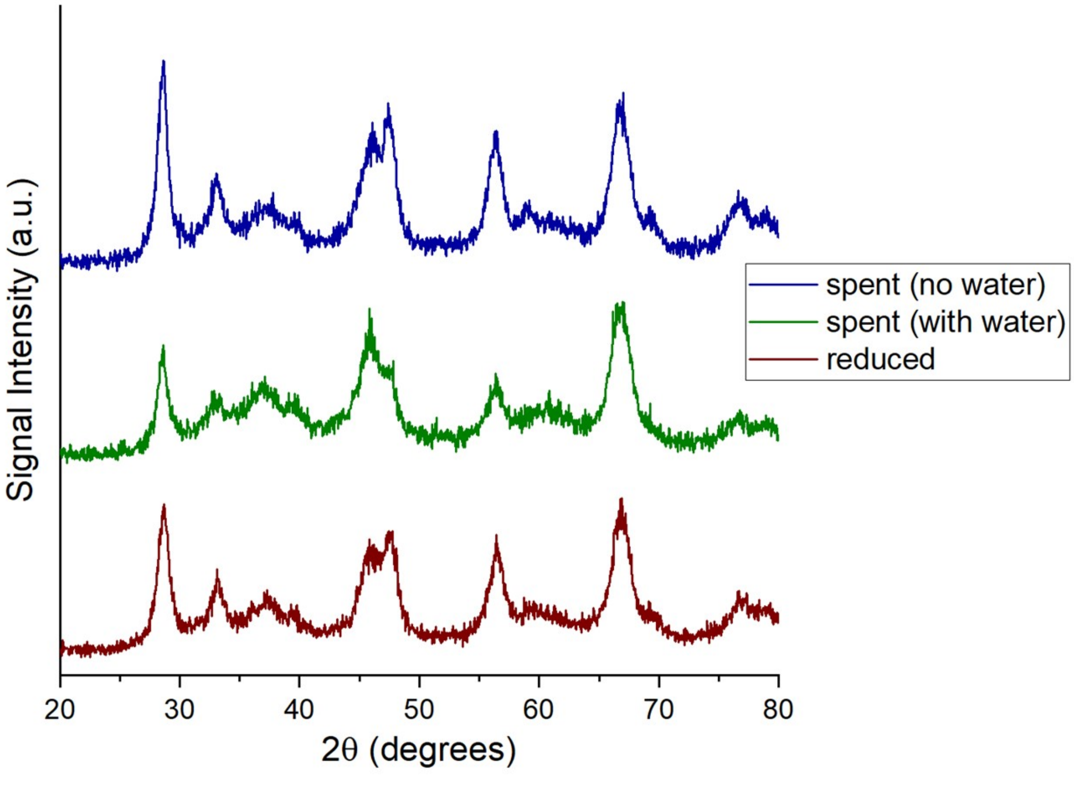


Figure S.4. X-ray diffraction spectra of reduced, spent with water, and spent without water of 10Ni15Ce catalysts.

Table S.1. XRD diffraction data

CeO$_2$ cubic Fm-3m		
Sample	d (nm)	Lattice parameter a (Å)
15Ce	9	5.431
10Ni15Ce	9	5.446
Spent 10Ni15Ce (no water)	11	5.428
Spent 10Ni15Ce (water)	12	5.546

Table S.2. Textural properties obtained from N$_2$ Physisorption

Sample	S_{BET} (m^2 g^{-1})	t-plot micropore area (m^2 g^{-1})	t-plot external surface area (m^2 g^{-1})	Avg. pore volume (cm^3 g^{-1})	Avg. pore diameter (nm)
Bare γ-alumina	185	10	175	0.506	8.6
10Ni	172	8	164	0.417	7.8
15Ce	165	2	163	0.399	7.7
10Ni15Ce	160	5	155	0.375	7.5
Spent 10Ni15Ce (no water)	158	4	154	0.339	7.2
Spent 10Ni15Ce (water)	147	11	135	0.354	7.9

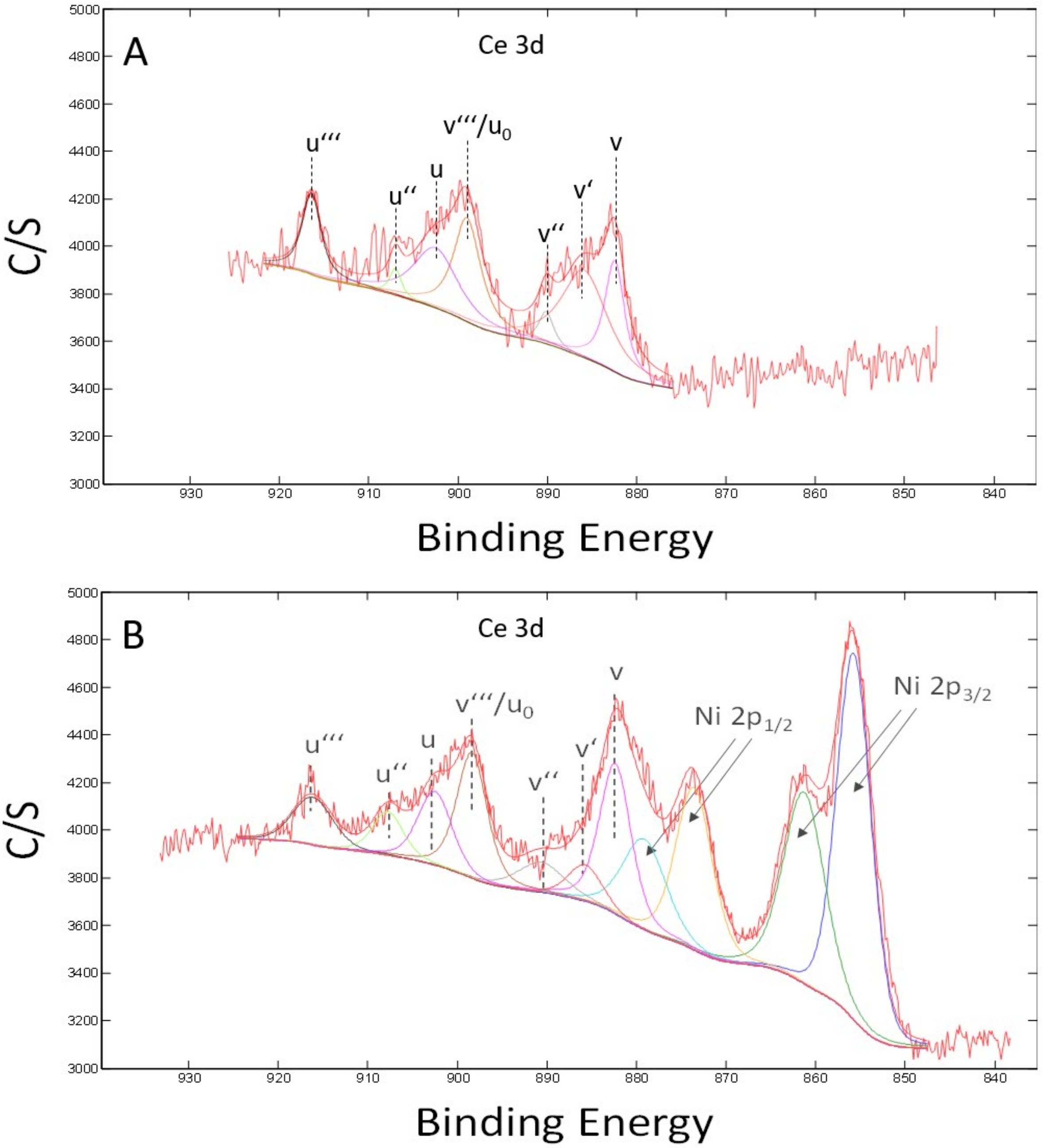


Figure S.5. XPS analysis of A) 15Ce catalyst and B) 10Ni15Ce catalyst

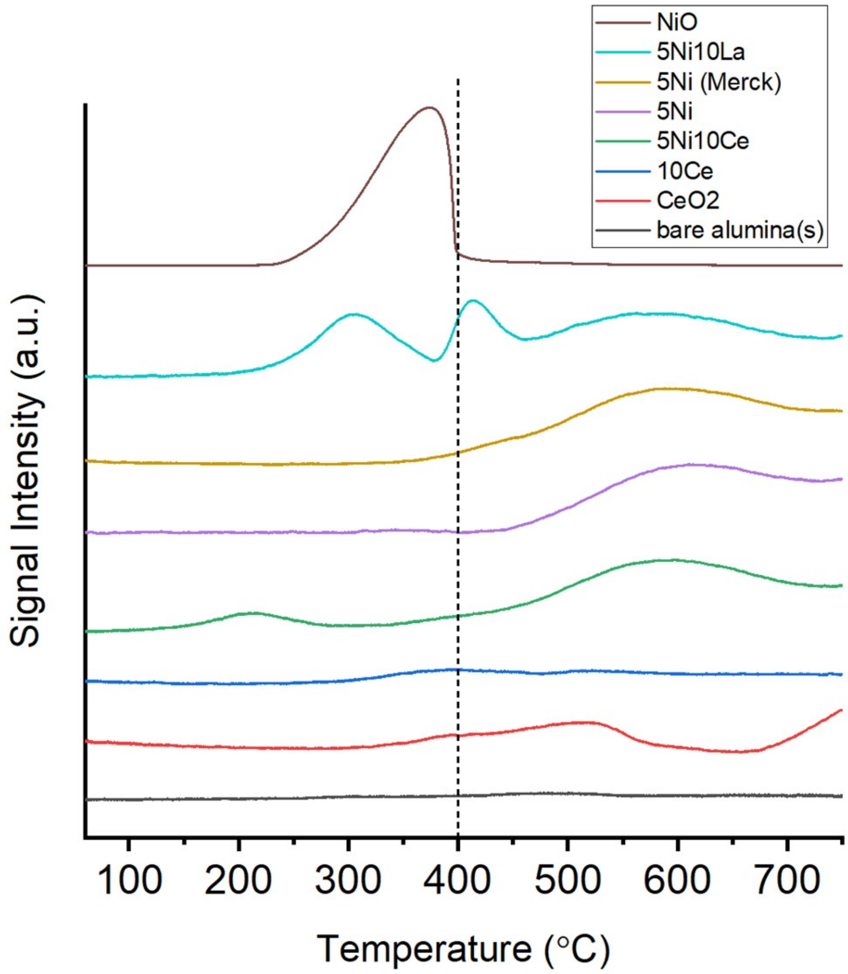


Figure S.6. Comparative H_2-TPR profiles of bare support, metal oxides, and doped γ-alumina supports.

Table S.3. Quantitative results for NH_3, CO, and CO_2 desorption and calculated concentration of sites.

Sample	Volume of NH_3 (mL)	Conc. Of Acidic sites (µmol g^{-1})	Volume of CO (mL)	Conc. Of Metallic sites (µmol g^{-1})	Degree of Dispersion (%)	Volume of CO_2 (mL)	Conc. Of Basic sites (µmol g^{-1})
Bare Spheralite	1.32	590	N/A	N/A	---	0.13	60
10Ni	1.11	502	0.15	65	3.9	0.16	70
10Ni15Ce	0.65	289	0.08	35	2.1	0.16	70
Spent 10Ni15Ce (no water)	0.50	222	0.14	61	3.7	0.34	152
Spent 10Ni15Ce (water)	0.56	240	0.09	41	2.4	0.32	135

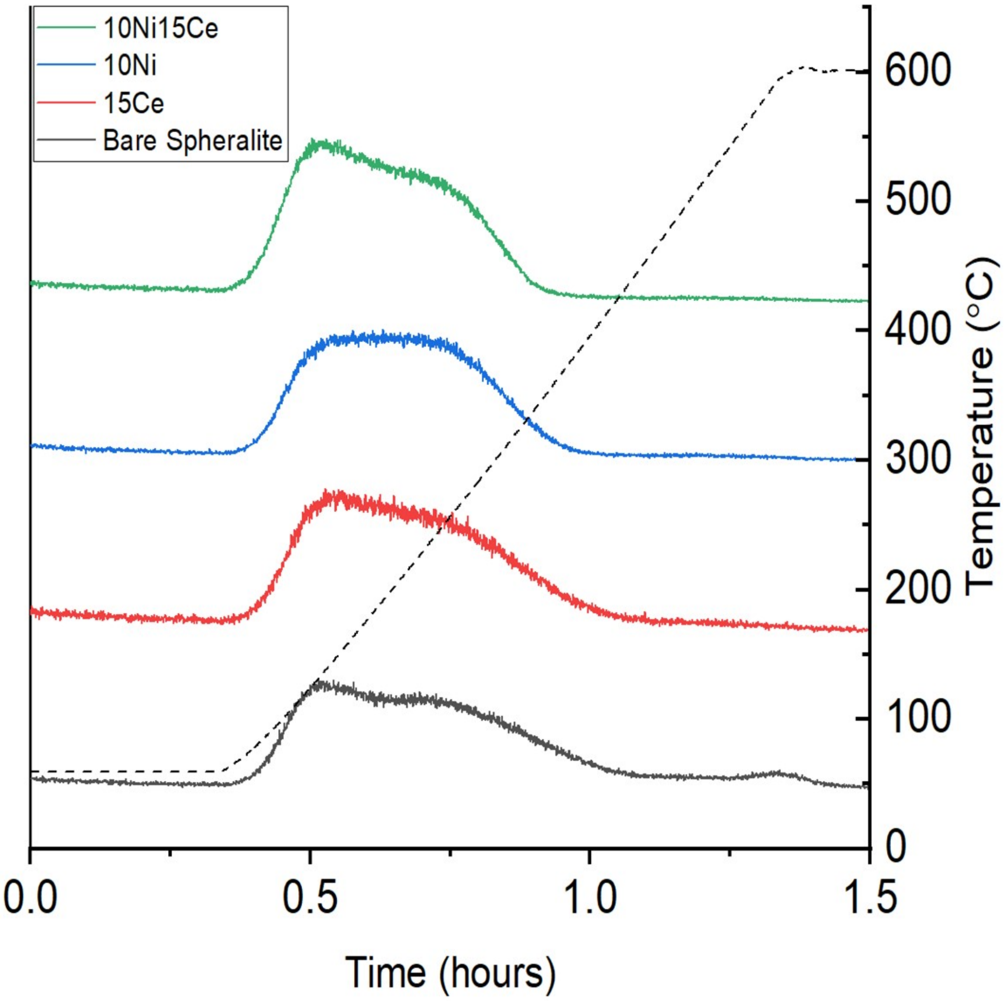


Figure S.7. NH_3-TPD-MS profiles for m/z = 15 of bare and doped γ-alumina catalysts.

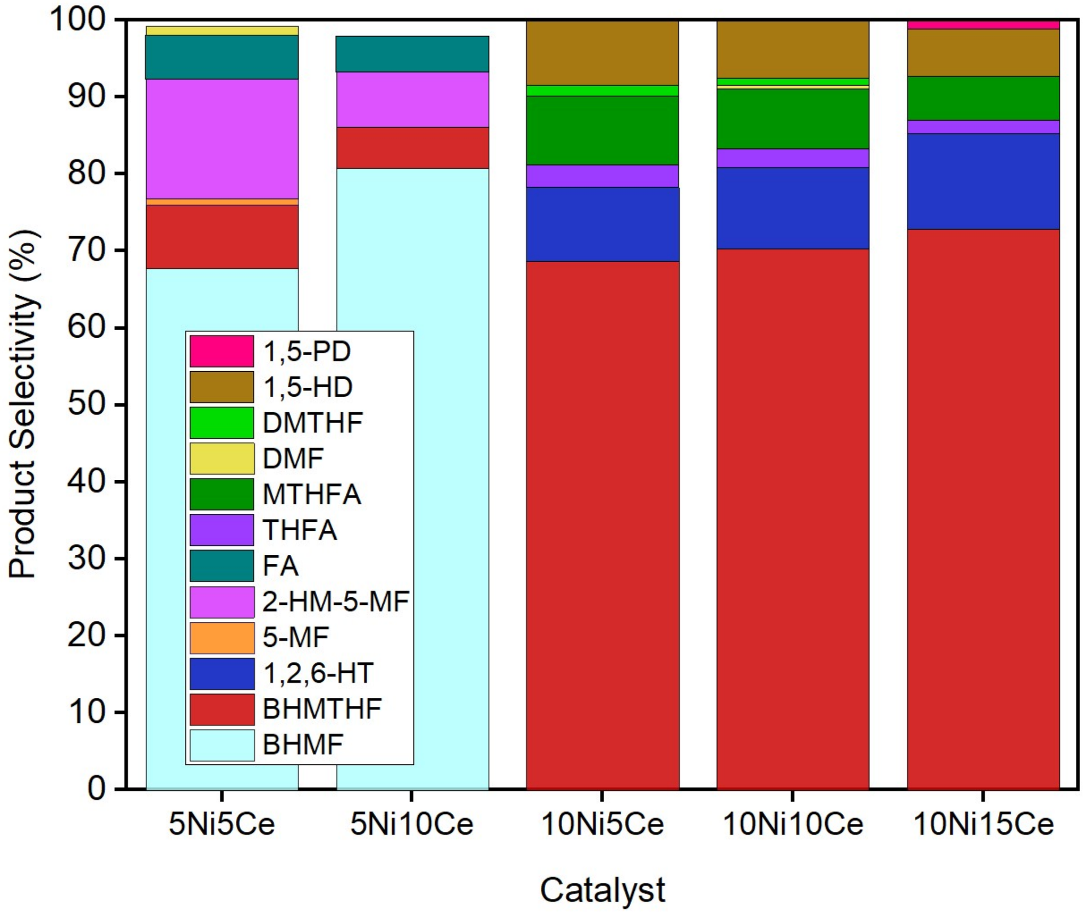
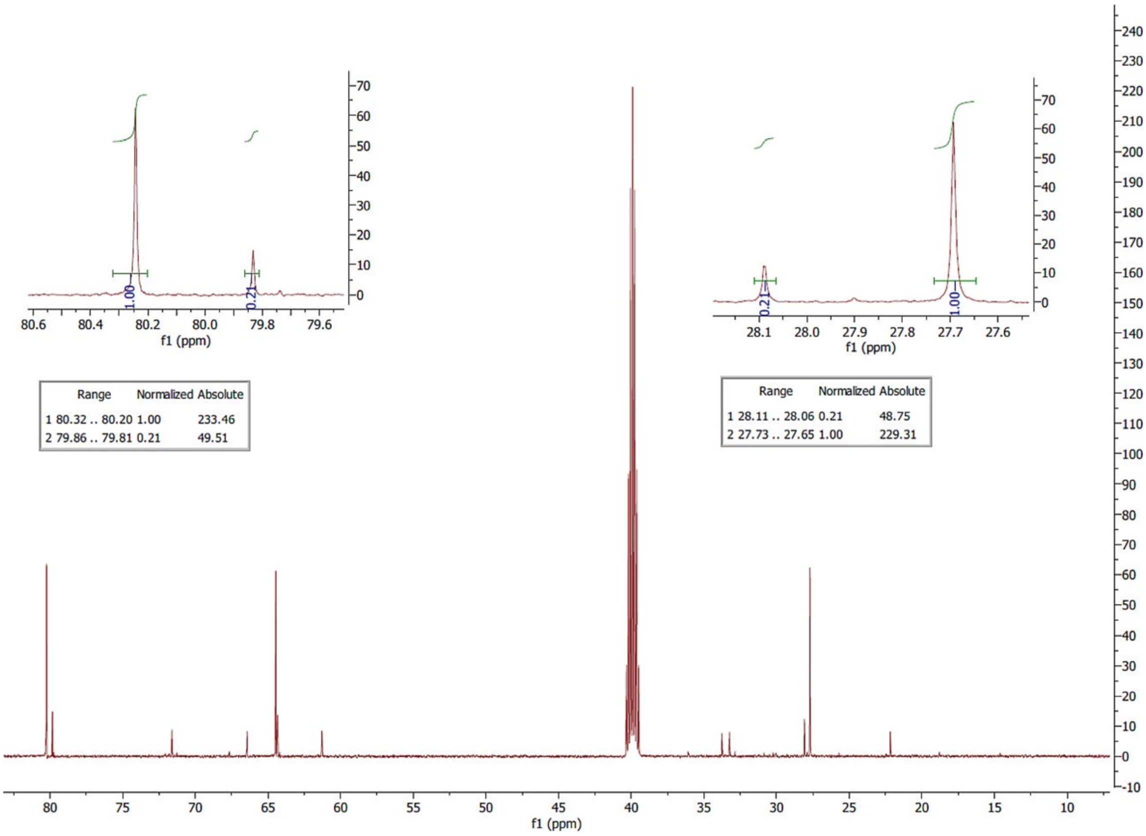


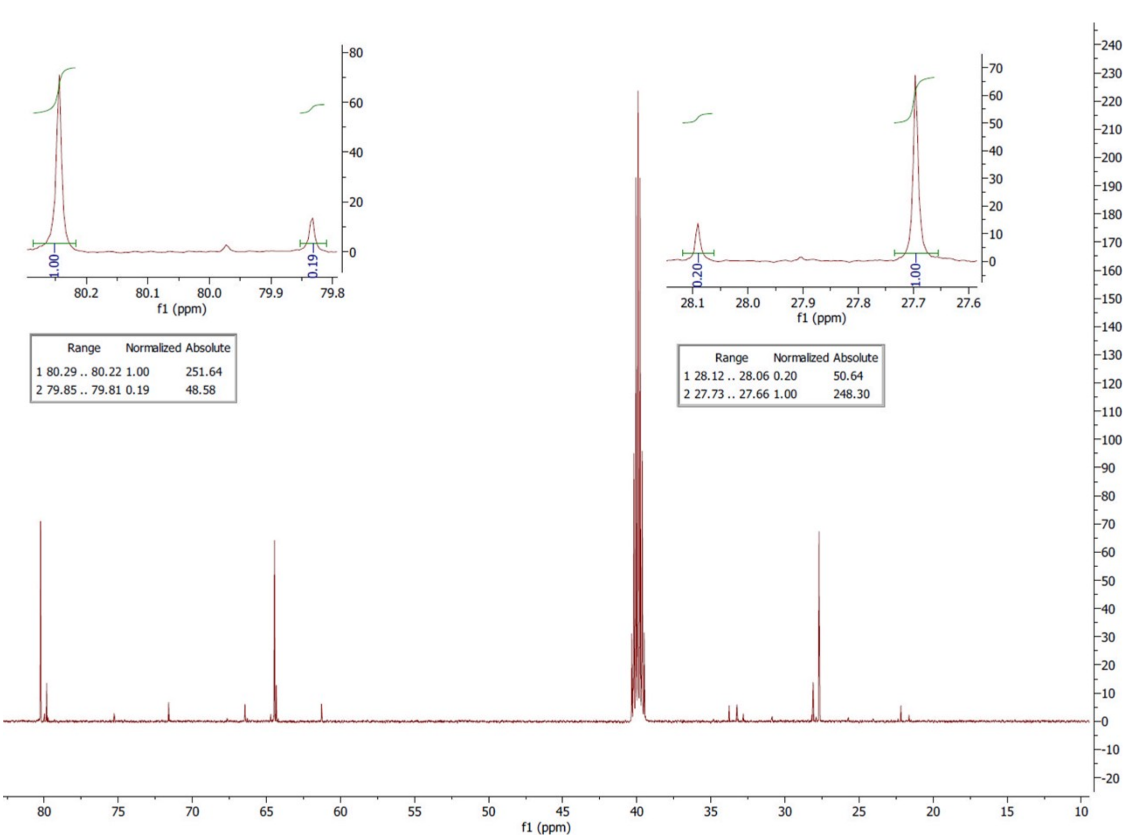
Figure S.8. Comparison of product selectivity between different loadings of Ni and Ce. (Reaction conditions: 200 °C, 50 bar of H_2, 3 hours, pure THF as solvent).



	Range	Normalized	Absolute
1	80.32 .. 80.20	1.00	233.46
2	79.86 .. 79.81	0.21	49.51

	Range	Normalized	Absolute
1	28.11 .. 28.06	0.21	48.75
2	27.73 .. 27.65	1.00	229.31

Figure S.9. ^{13}C NMR spectrum in d_6-DMSO of final reaction mixture using 10Ni15Ce at 200 °C in THF:water. Trans-BHMTHF displays peaks at 79.83 and 28.08 ppm and cis-BHMTHF displays peaks at 80.26 ppm and 27.69 ppm indicating an average cis:trans ratio of 4.71 (compared to 4.8 from GC analysis). These peaks correspond well with what has been reported elsewhere.[1,2]



	Range	Normalized	Absolute
1	80.29 .. 80.22	1.00	251.64
2	79.85 .. 79.81	0.19	48.58

	Range	Normalized	Absolute
1	28.12 .. 28.06	0.20	50.64
2	27.73 .. 27.66	1.00	248.30

Figure

S.10. ^{13}C NMR spectrum in d_6-DMSO of final reaction mixture using 10Ni15Ce at 190 °C in pure THF. Trans-BHMTHF displays peaks at 79.83 and 28.09 ppm and cis-BHMTHF displays peaks at 80.26 ppm and 27.73 ppm indicating an average cis:trans ratio of 5.04 (compared to 5.1 from GC analysis). These peaks correspond well with what has been reported elsewhere.[1,2]

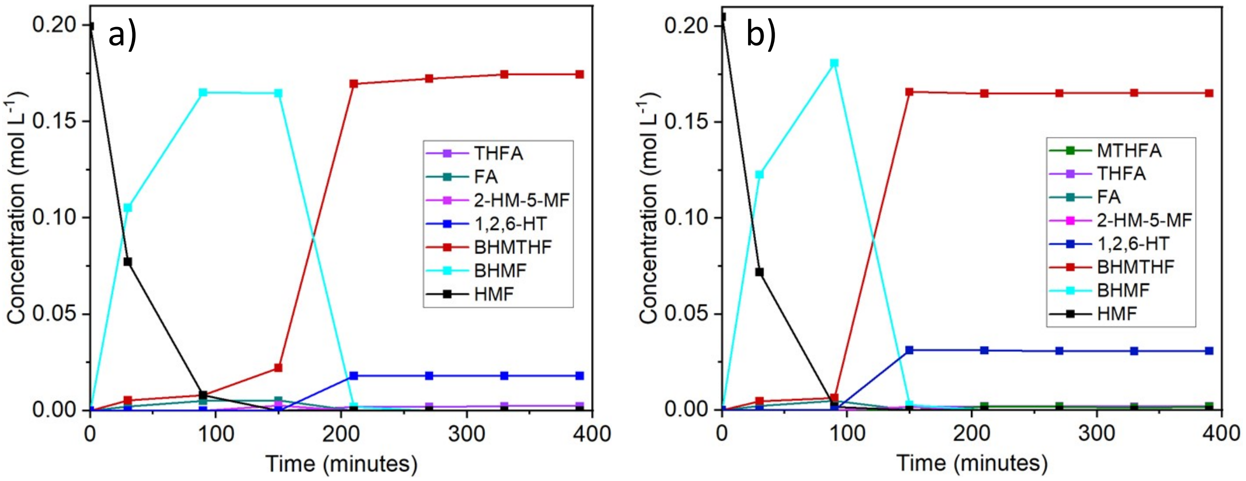


Figure S.11. a) 100mg of 10Ni catalyst, 190 °C, 50 bar of H_2, 5 vol.% water in THF as solvent. b) 100 mg of 10Ni and 100mg of 15Ce catalysts separately, 190 °C, 50 bar of H_2, 5 vol.% water in THF as solvent.

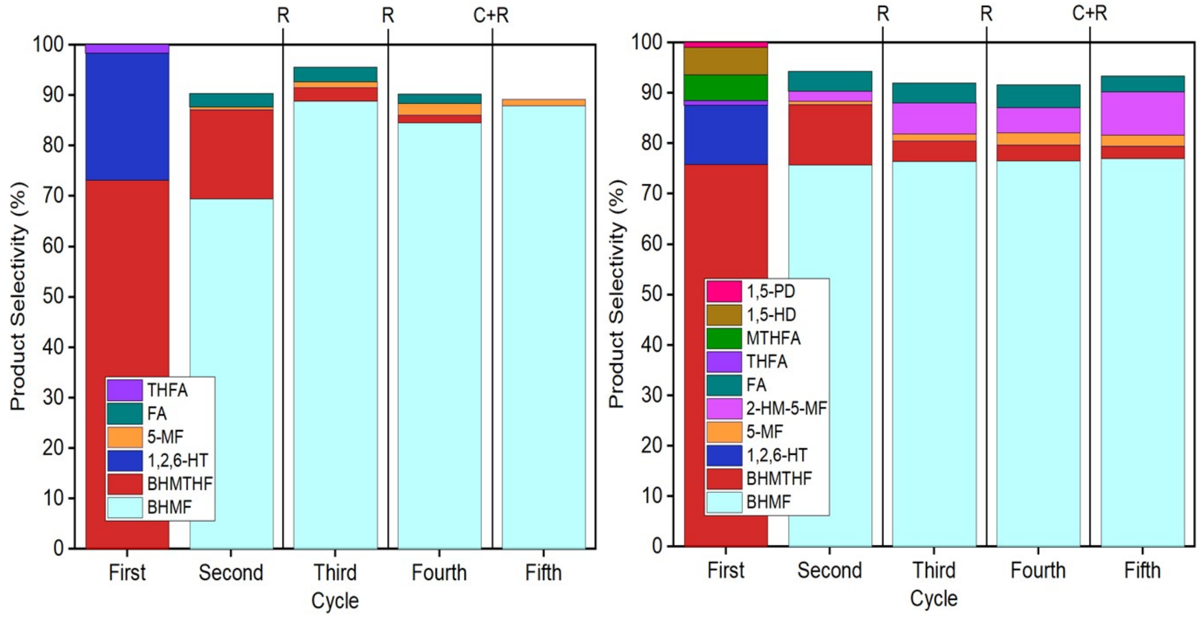


Figure S.12 a) Recyclability tests of 10Ni15Ce catalyst with (left) and without (right) water. R = reduction treatment was performed, C+R = calcination + reduction treatment was performed.

References

1 A. Cadu, K. Sekine, J. Mormul, D. M. Ohlmann, T. Schaub and A. S. K. Hashmi, *Green Chem.*, 2018, **20**, 3386–3393.

2 S. H. Krishna, D. J. McClelland, Q. A. Rashke, J. A. Dumesic and G. W. Huber, *Green Chem.*, 2017, **19**, 1278–1285.