

# Heterogeneous Fenton-type Oxidative Degradation of Low Density Polyethylene to Valuable Acid Products Using a Nanostructured Fe-CeO<sub>2</sub> Solid Solution Catalyst

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## Supporting Information

### Experimental

#### Chemicals and Materials

Hydrogen peroxide (30%), nitric acid (65%), iron (III) chloride (FeCl<sub>3</sub>·4H<sub>2</sub>O), cerium (IV) sulfate (Ce(SO<sub>4</sub>)<sub>2</sub>), cerium oxide nano powder, and sodium hydroxide pellets (NaOH) were all purchased from Sigma Aldrich. LDPE powder (500 um), with a density of 0.91-0.96 gml<sup>-1</sup> was purchased from Thermo Fischer.

**CeO<sub>2</sub> reference:** CeO<sub>2</sub> nano powder was calcinated at 450 °C for 4h and used without any further treatment.

**Fe<sub>2</sub>O<sub>3</sub> reference:** 2 g FeCl<sub>3</sub>·4H<sub>2</sub>O was added to a round bottom flask along with 50 mL deionised H<sub>2</sub>O. The mixture was stirred at room temperature for 10 minutes before the pH was adjusted to 12 using 1 M NaOH solution. When the desired pH was achieved and a rusty brown precipitate had crashed out, mixture was refluxed for 2 h at 100 °C under N<sub>2</sub> with stirring. The solid Fe<sub>2</sub>O<sub>3</sub> particles were then collected by suction filtration and dried in an oven at 75 °C overnight. The resulting solid was then calcinated at 450 °C for 4 h.<sup>1</sup>

**Fe-CeO<sub>2</sub> 1:1 solid solution:** A solution of 0.755 g FeCl<sub>3</sub> in 25 mL DI H<sub>2</sub>O and 1.933 g Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in 25 mL DI H<sub>2</sub>O were combined to form a 1:1 molar ratio of Fe:Ce and stirred at room temperature for 10 minutes before the pH was adjusted to 12 using 1 M NaOH solution and a red/brown precipitate appeared. The mixture was refluxed for 2 h at 100 °C under N<sub>2</sub> with stirring. The resulting particles

were collected by suction filtration and dried in an oven at 75 °C overnight. The solid was then calcinated at 450 °C under air for 4h. For different Fe:Ce ratios, the masses of salt precursors were adjusted accordingly.

**Fe-Ce 1:2:** A solution of 0.378 g FeCl<sub>3</sub> in 25 mL DI H<sub>2</sub>O and 0.2M 1.933 g Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in 25 mL DI H<sub>2</sub>O were combined to form a 1:2 molar ratio of Fe:Ce and synthesis method was continued as above.

**Fe-Ce 2:1:** A solution of 0.755 g FeCl<sub>3</sub> in 25 mL DI H<sub>2</sub>O and 0.967 g Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in 25 mL DI H<sub>2</sub>O were combined to form a 2:1 molar ratio of Fe:Ce and synthesis method was continued as above.

### **Oxidative Degradation of LDPE to Carboxylic Acids:**

0.3 - 0.5 g LDPE, catalyst loadings of 1 – 30 wt. % and 10 mL of H<sub>2</sub>O<sub>2</sub> solutions from 3 – 15 % (w/w) were added to a Milestone Flexiwave high pressure SK-15 Teflon vessel along with a stir bar. For a 15 % H<sub>2</sub>O<sub>2</sub> solution, 5 mL of Millipore H<sub>2</sub>O and 5 mL 30 % (w/w) H<sub>2</sub>O<sub>2</sub> were added to the vessel. The H<sub>2</sub>O<sub>2</sub> was added last to minimise peroxide degradation prior to the reaction. Typical reaction conditions were a 10 min ramp time, 3 h hold at 180 °C, stir speed 1800 rpm using a crosshair stir bar, and 1200 W upper power limit (reactions only typically required ~300 W). Once the reaction was complete and had cooled, it was Buchner filtered to separate the catalyst and any unreacted LDPE from the product mixture. The mass loss of LDPE was calculated by the equation below.

$$\text{Mass Loss LDPE} = \frac{W_0 - W_1}{W_0} \times 100 \%$$

Where  $W_0$  is the initial weight of LDPE added to the reaction and  $W_1$  is the weight of unreacted LDPE after the reaction. The product mixture was characterised by HPLC.

### **HPLC Analysis of Products**

The product mixture was analysed using an Agilent 1200 HPLC coupled to a UV detector (210 nm). 500 uL of product mixture was added to 500 uL of mobile phase to give a dilution factor of 2. The column used was an Agilent Hi-Plex H (300 x 7.7 mm) size exclusion column. The mobile phase was 2.5 mM sulfuric acid at a flow rate of 0.5 mLmin<sup>-1</sup> and the temperature was set to 50 °C, following Bäckström et al.'s method and the column specifications.<sup>2</sup> The concentration of each product present in the sample was then calculated against calibration curves that were made by standards of

carboxylic acids: succinic, formic, glutaric, acetic, adipic, propionic, butyric and pimelic acid. The yield was calculated relative to the initial weight of LDPE as shown below.

*Mass of end product (g) = Conc of end product (g L<sup>-1</sup>) x reaction volume (L)*

$$\text{Yield of Organic Products (\%)} = \frac{\text{Mass of end products (g)}}{\text{Mass of starting material (g)}} \times 100 \%$$

## Materials Characterisation

Raman spectroscopy was performed using an Oceanview InVia Raman Spectrometer using a 25 mW Ar-ion laser under 532 nm excitation. The beam was focused onto the samples using a 50x objective lens and spectra were collected using a RenCam CCD camera.

X-ray Diffraction (XRD) was carried out on a PANalytical X'Pert PRO with Cu K $\alpha$  radiation and a constant step of 0.0098° 2 $\theta$  and a counting time of 149.97 seconds per step. Crystallite size was calculated by the Scherrer equation shown below.

$$D_{hkl} = \frac{k\lambda}{B_{hkl}\cos\theta_{hkl}}$$

Where  $D_{hkl}$  is the crystallite size perpendicular to the hkl plane, k is a constant (0.9) for spherical samples with cubic symmetry,  $\lambda$  is the wavelength of x-ray radiation,  $B_{hkl}$  is the full width at half maximum (FWHM) of the hkl diffraction peak and  $\theta_{hkl}$  is the Bragg angle of the (hkl) peak. It is worth commenting that there is limited accuracy with the Scherrer equation for smaller crystallite sizes due to factors such as strain, instrument broadening and shape effects, however for the purpose of this study, it can be used to support other analysis methods.

X-ray Photoelectron Spectroscopy (XPS) was carried out using a KRATOS ACIS 165 monochromatized X-ray photoelectron spectrometer equipped with an Al K $\alpha$  (hv = 1486.6 eV) X-ray source. Spectra were collected at a take-off angle of 90 ° and all spectra were referenced to the C 1s peak at 284.8 eV. The quantitative data of Ce<sup>4+</sup> and Ce<sup>3+</sup> in CeO<sub>2</sub> and each of the solid solutions were calculated using the expressions as reported by Suresh et al.<sup>3</sup>

$$\% \text{Ce}^{3+} = \frac{A_{\text{Ce}^{3+}}}{A_{\text{Ce}^{3+}} + A_{\text{Ce}^{4+}}} \times 100\%$$

$$\% Ce^{4+} = \frac{A_{Ce^{4+}}}{A_{Ce^{3+}} + A_{Ce^{4+}}} \times 100\%$$

Where  $A_{Ce^{3+}} = v_0 + v' + u_0 + u'$  and  $A_{Ce^{4+}} = v + v'' + v''' + u + u'' + u'''$  are the sum of the areas of the fitted peaks corresponding to  $Ce^{3+}$  and  $Ce^{4+}$ .

Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded on a Perkin Elmer Spectrum Two FT-IR Spectrometer operating in the range of 4000-450  $cm^{-1}$  with a resolution of 4  $cm^{-1}$  and spectra were averaged from 20 scans. The carbonyl index was estimated using the SAUB method as outlined by Almond et al<sup>4</sup>

$$Carbonyl\ Index\ (CI) = \frac{Area\ under\ band\ \sim\ 1748\ cm^{-1}}{Area\ under\ band\ \sim\ 1465\ cm^{-1}}$$

Total reflection X-ray fluorescence spectroscopy was (TXRF) was carried out using an S2 Picofox TXRF Spectrometer with a scan time of 250 s. Quantification using an internal standard and correlating concentration of analyte with relative sensitivities to the net intensities of the analyte and the Ni internal standard was calculated by the following equation<sup>5</sup>:

$$C_A = \frac{\frac{N_A}{S_A}}{\frac{N_{IS}}{S_{IS}}} \times C_{IS}$$

Where  $C_A$  and  $C_{IS}$  are the concentrations of the analyte and the IS, respectively.  $N_A$  and  $N_{IS}$  refer to the net intensities of the analyte and the internal standard, and  $S_A$  and  $S_{IS}$  are the relative sensitivities of the analyte and internal standard, respectively.

Scanning electron microscopy (SEM) and EDS mapping was performed on a Zeiss Supra 40 high resolution SEM at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) analysis was performed using a FEI Titan TEM, at an operating voltage of 300 kV.

Supporting Figures:

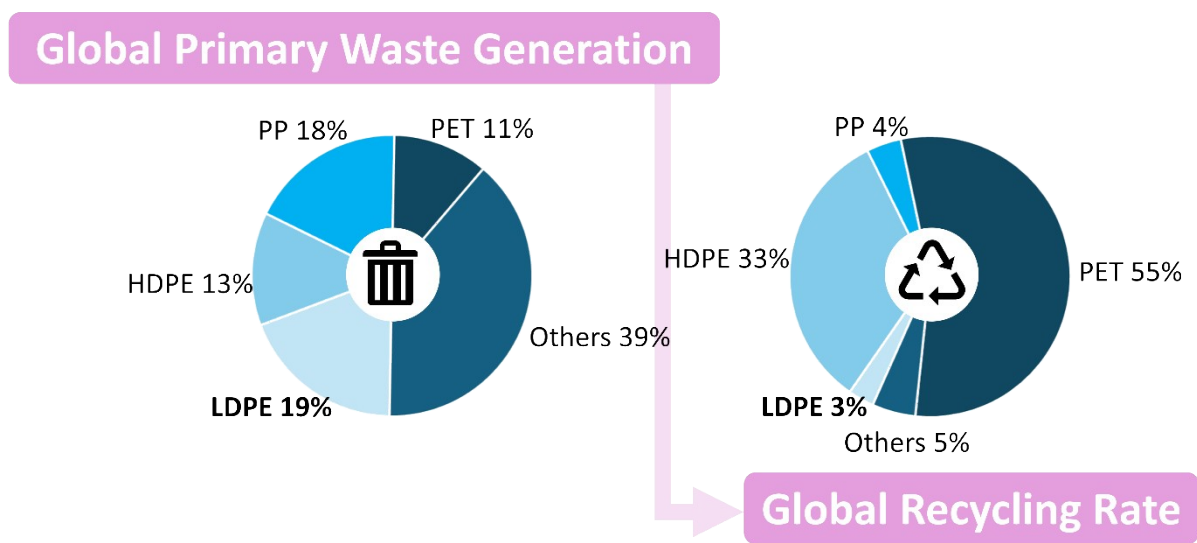
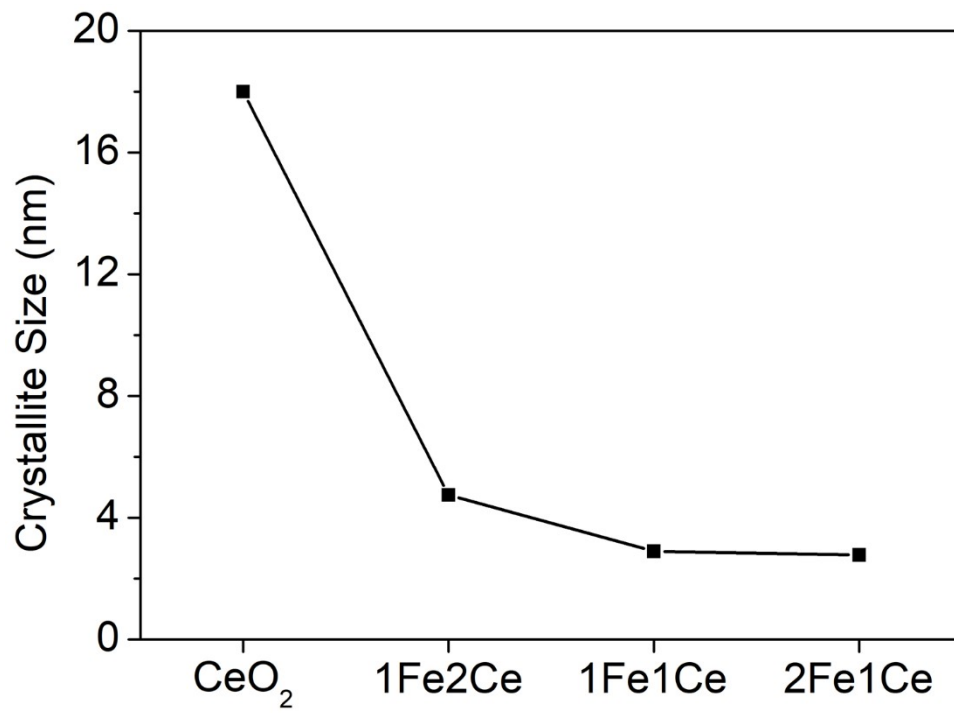
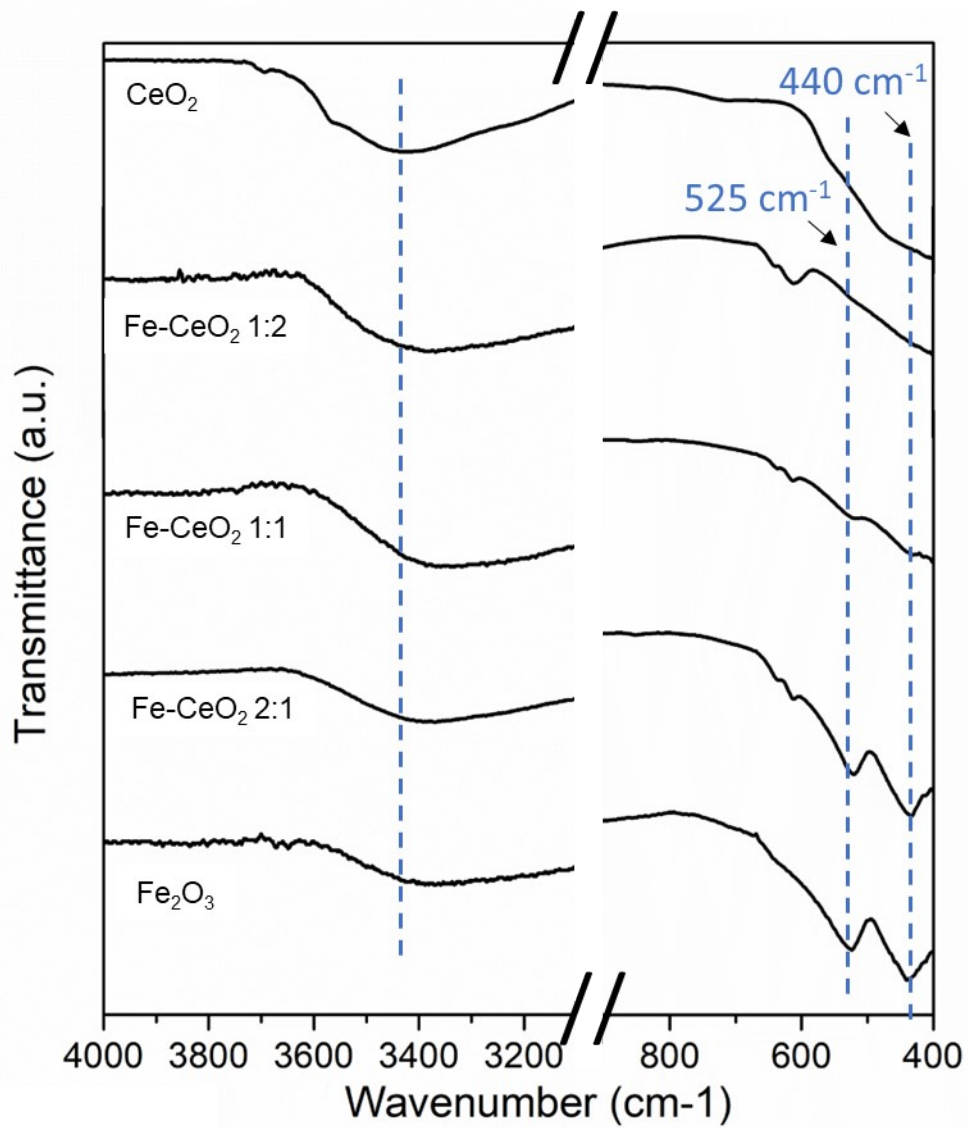


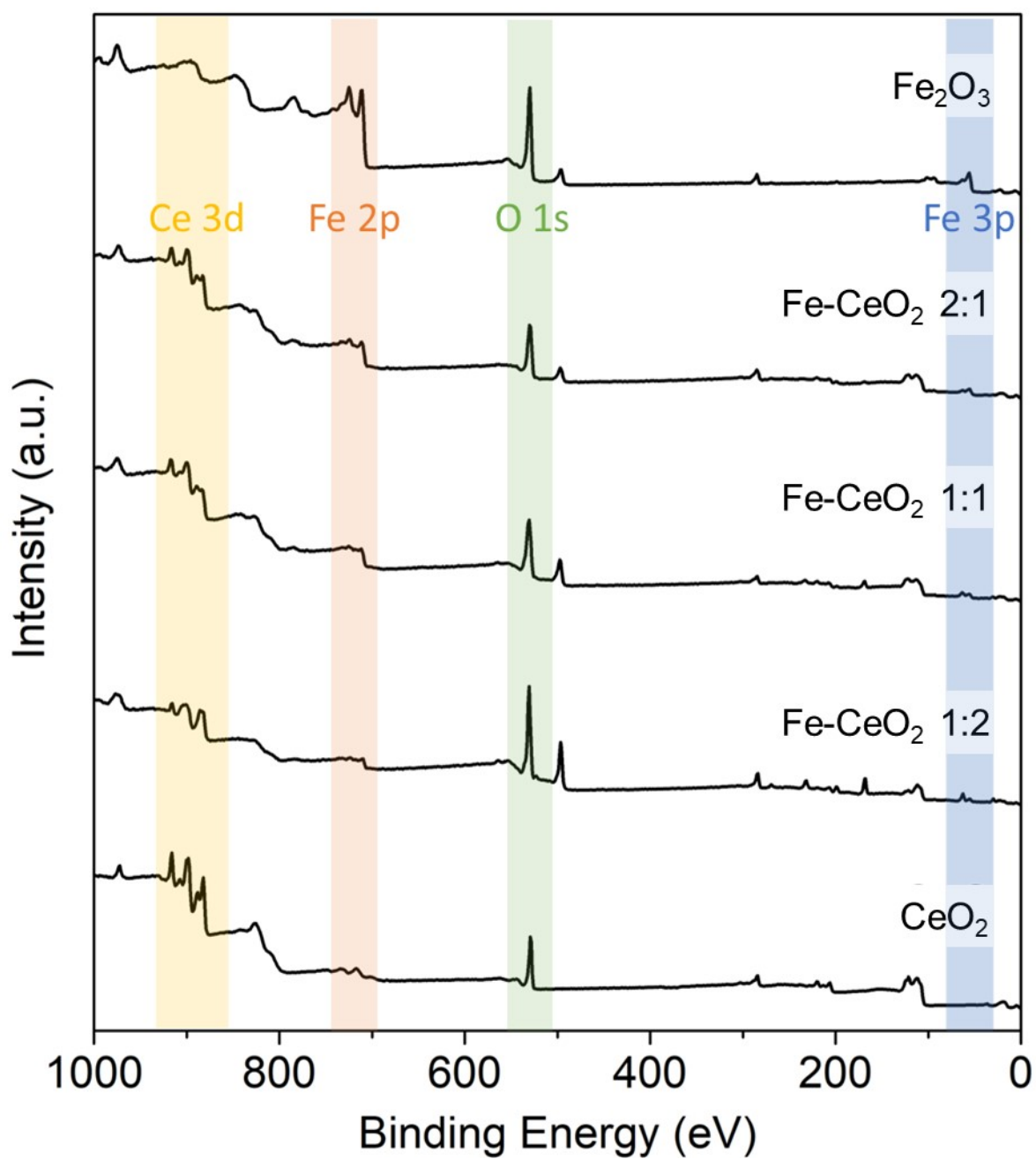
Figure S1: a) Global primary waste generation<sup>6</sup>, b) Global recycling rate by polymer type.<sup>7</sup>



**Figure S2:** Decreasing crystallite size with increasing Fe content as calculated by Scherrer equation.

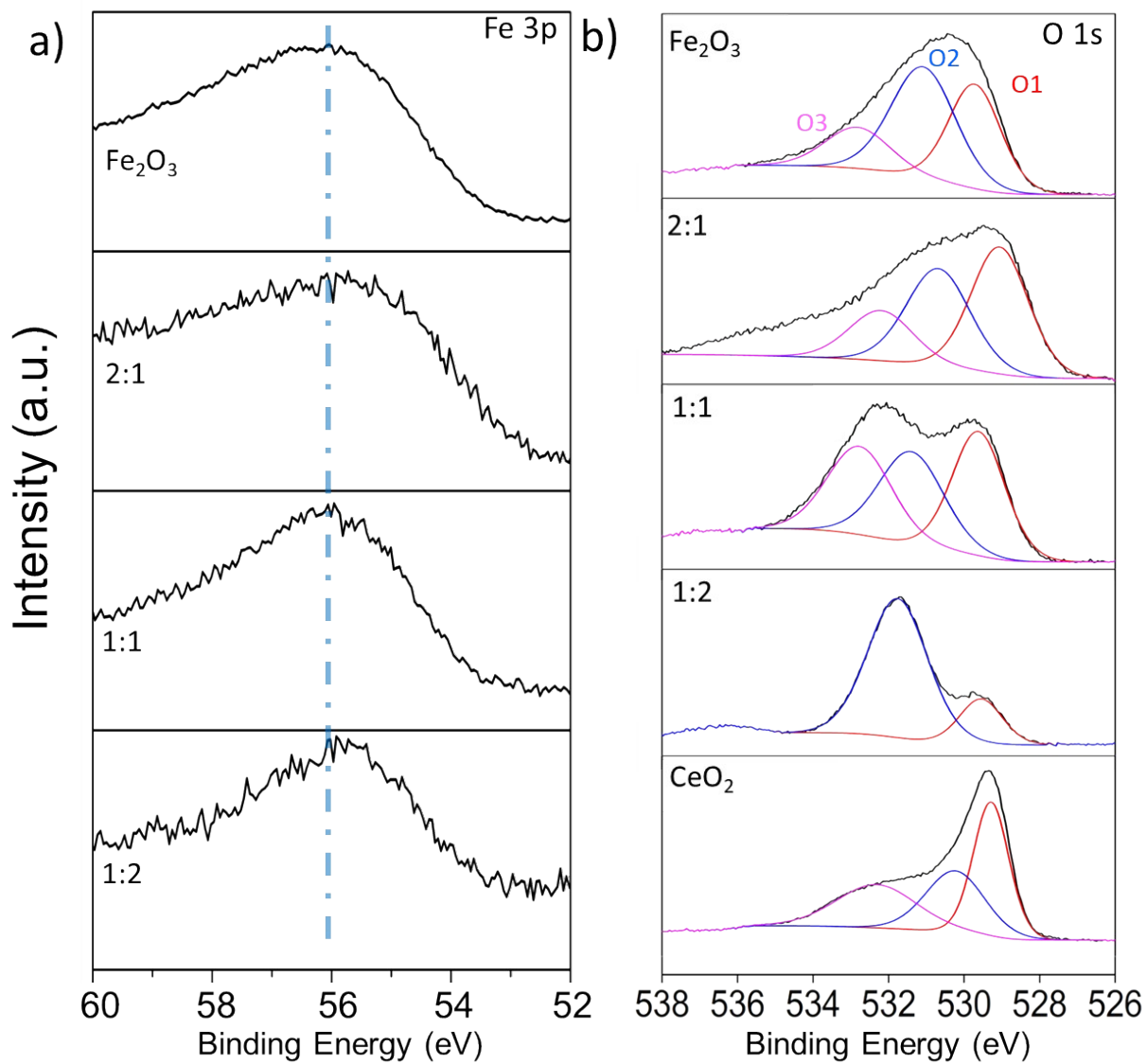


**Figure S3:** FTIR of CeO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and each of the Fe-CeO<sub>2</sub> solid solution catalysts.

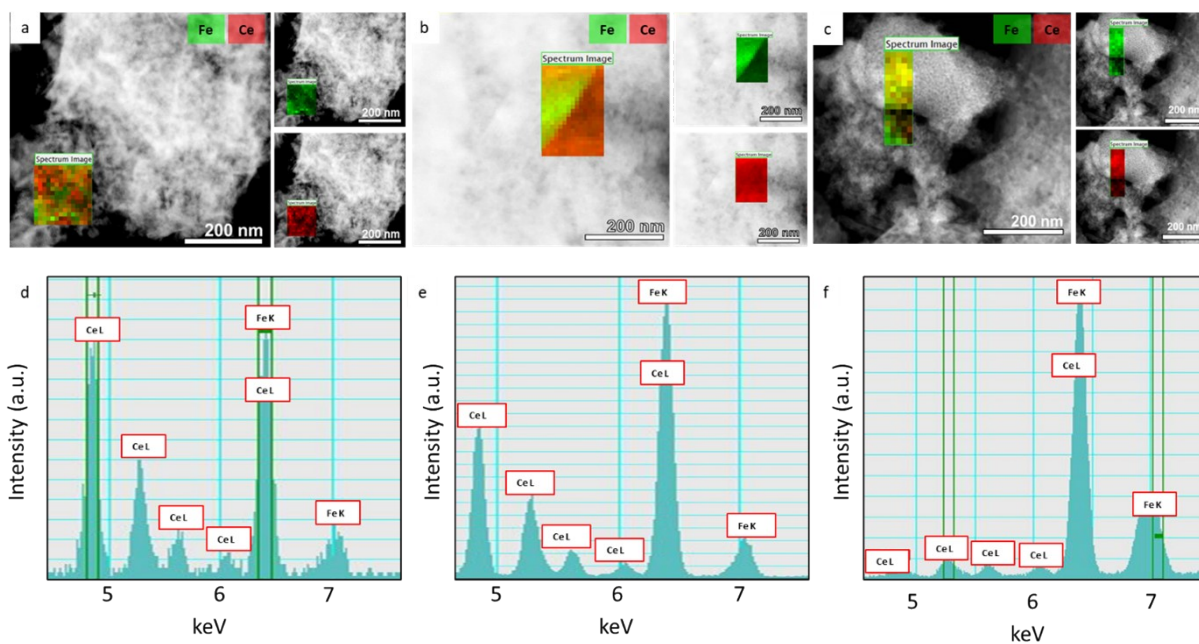


**Figure S4:** XPS Survey scans for Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and each of the Fe-CeO<sub>2</sub> solid solution catalysts.

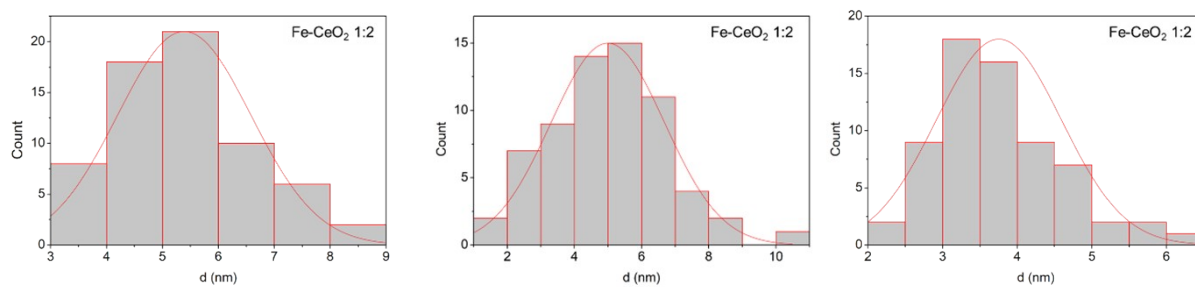




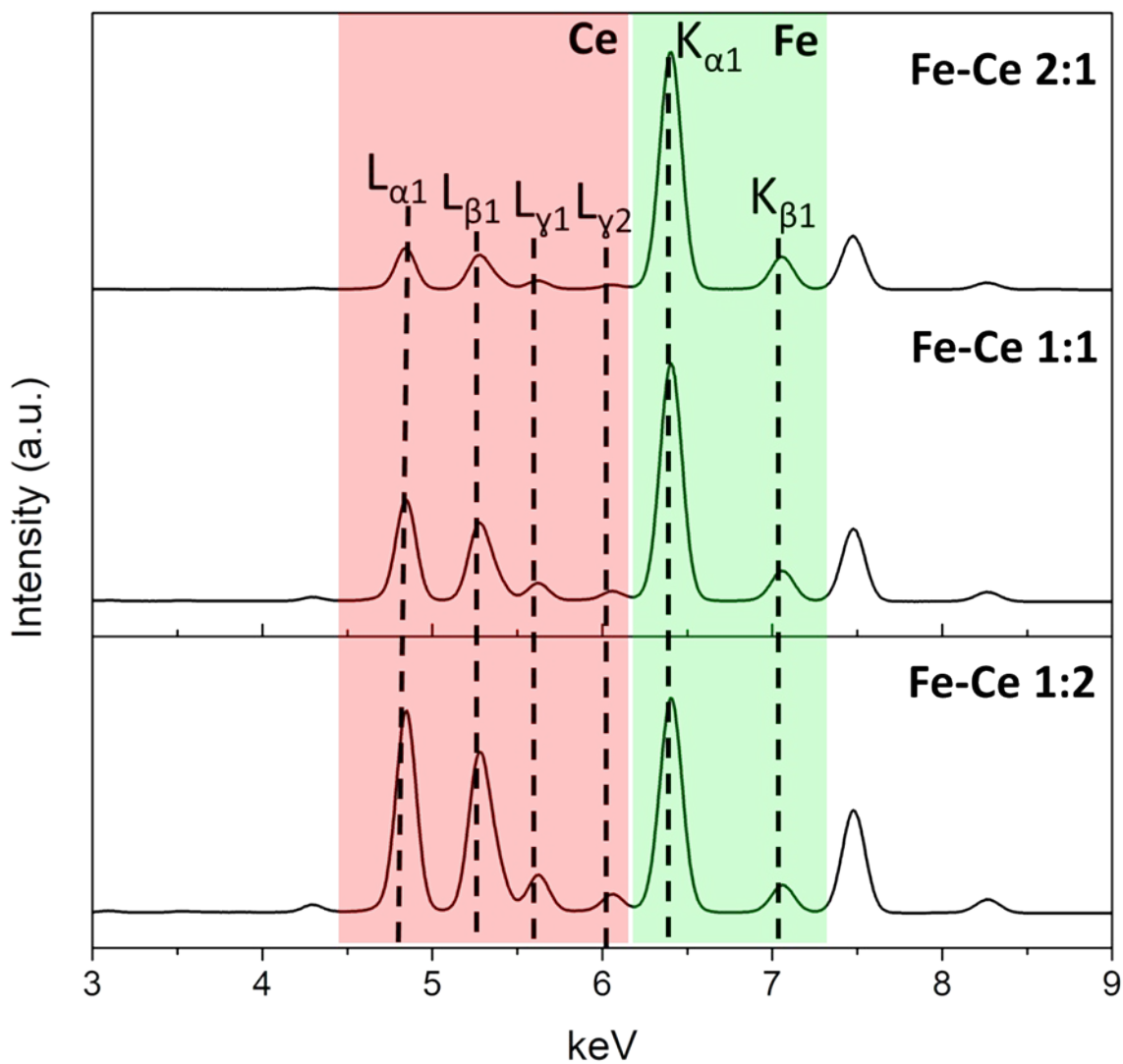
**Figure S5:** a) Fe 3p XPS for  $\text{Fe}_2\text{O}_3$  and the Fe-CeO<sub>2</sub> solid solutions and b) O 1s XPS for  $\text{Fe}_2\text{O}_3$ , CeO<sub>2</sub> and the Fe-CeO<sub>2</sub> solid solutions.



**Figure S6:** HAADF & EDX of a) Fe-CeO<sub>2</sub> 1:2, b) Fe-CeO<sub>2</sub> 1:1 and c) Fe-CeO<sub>2</sub> 2:1 and d)-f) corresponding EDX spectra.



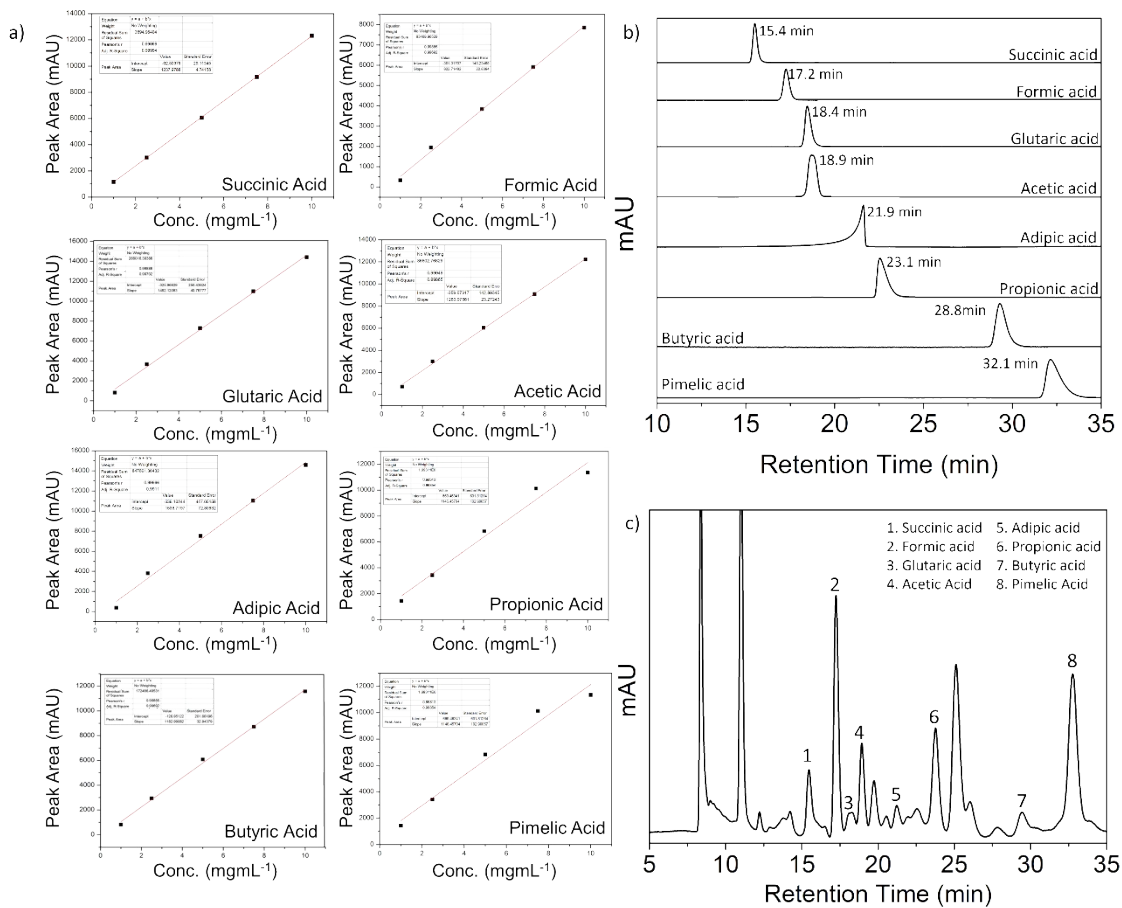
**Figure S7:** Size distribution histograms of the Fe-CeO<sub>2</sub> 1:2, 1:1 and 2:1 catalysts.



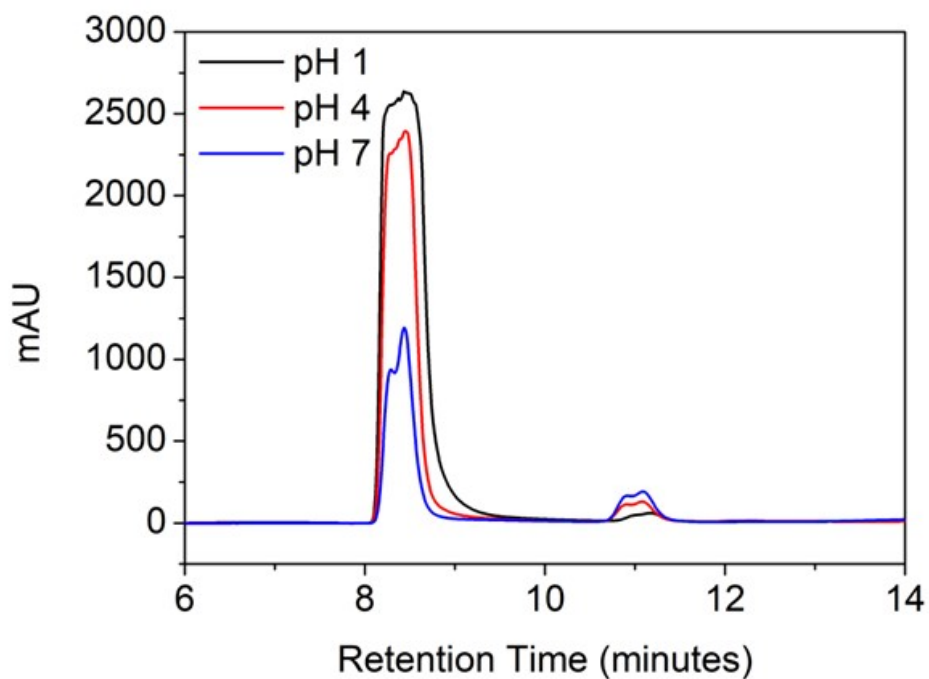
**Figure S8:** TXRF Spectra of the Fe-CeO<sub>2</sub> catalysts. (Ni IS peaks at 7.4 keV and 8.3 keV)

**Table S1:** Quantification from TXRF.

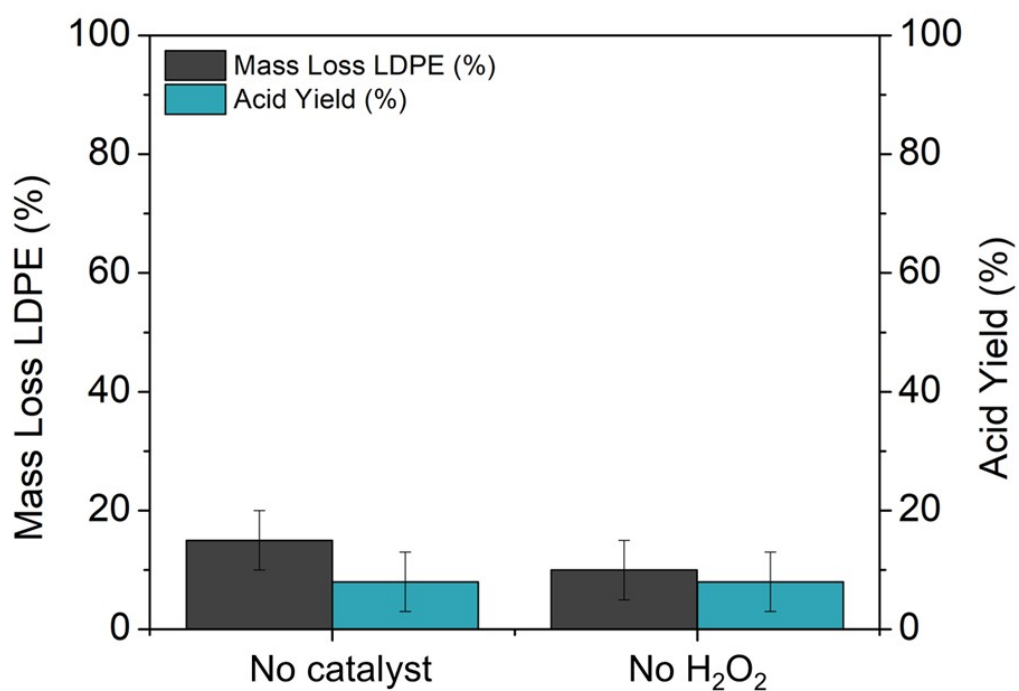
Catalyst	Element	(gL <sup>-1</sup> )	(molL <sup>-1</sup> )	Molar Ratio
Fe-CeO <sub>2</sub> 2:1	Fe	3.0703	0.055	2:1
	Ce	3.4933	0.025	
Fe-CeO <sub>2</sub> 1:1	Fe	2.2296	0.040	1:1
	Ce	5.9871	0.042	
Fe-CeO <sub>2</sub> 1:2	Fe	1.3937	0.025	1:2
	Ce	8.536	0.060	



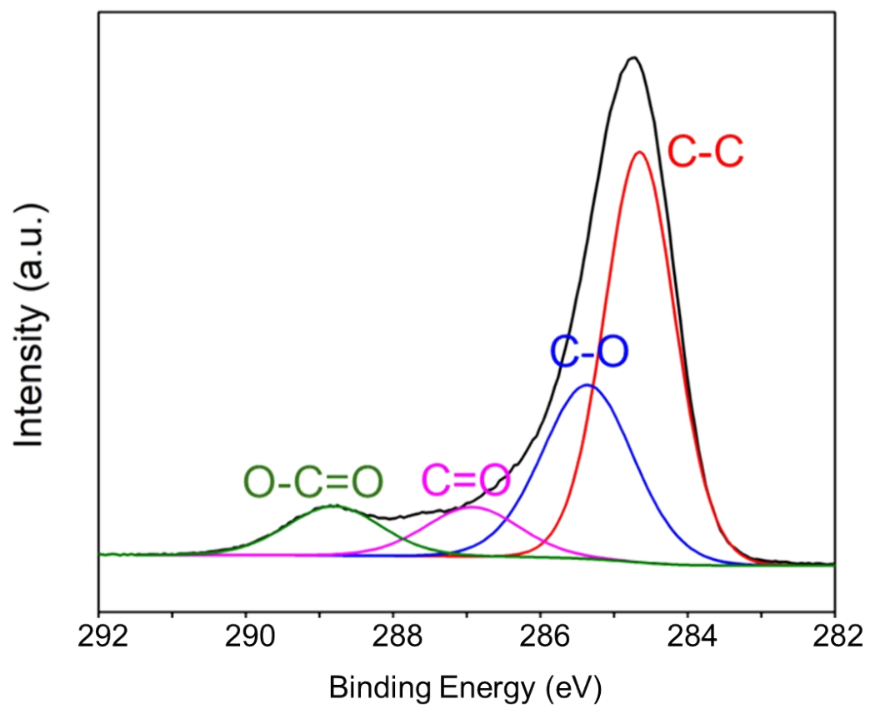
**Figure S9:** a) Calibration curves for each of the acid standards, b) retention times of the acid standards, c) typical chromatogram of LDPE degradation products.



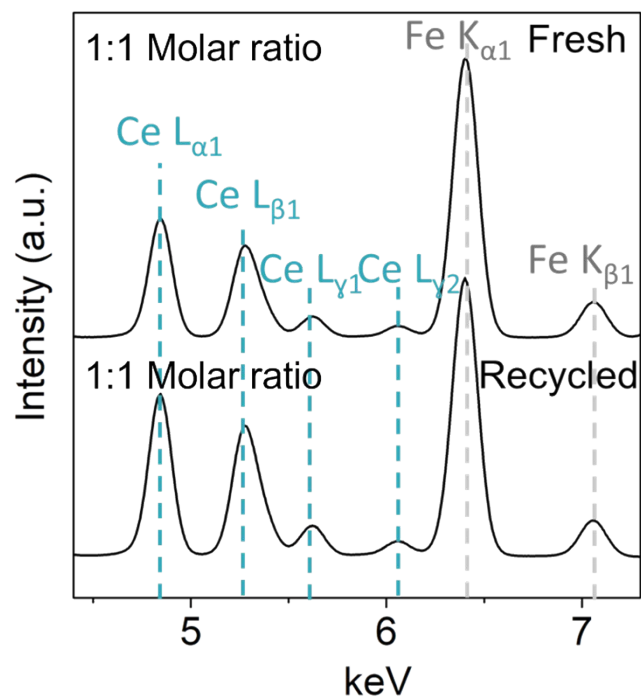
**Figure S10:** HPLC chromatograms at pH1, 4 and 7 showing nitrate peak.



**Figure S11:** Reaction results with no catalyst (0.5 g LDPE, 10 mL 15 % (w/w) H<sub>2</sub>O<sub>2</sub>) and no peroxide (0.5 g LDPE, 1 wt. % catalyst, 10 mL H<sub>2</sub>O).



**Figure S12:** C1s XPS core level of residual LDPE after 3 h of reaction time.



**Figure S13:** TXRF analysis of Fresh and Recycled Fe-CeO<sub>2</sub> catalyst.

## References:

1. M. Farahmandjou and F. Soflaee, *Physical Chemistry Research*, 2015, **3**, 191-196.
2. E. Bäckström, K. Odelius and M. Hakkarainen, *Industrial & Engineering Chemistry Research*, 2017, **56**, 14814-14821.
3. R. Suresh, V. Ponnuswamy and R. Mariappan, *Applied Surface Science*, 2013, **273**, 457-464.
4. J. Almond, P. Sugumaar, M. N. Wenzel, G. Hill and C. Wallis, 2020, **20**, 369-381.
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6. T. Thiounn and R. C. Smith, *Journal of Polymer Science*, 2020, **58**, 1347-1364.
7. L. Wimberger, G. Ng and C. Boyer, *Nature Communications*, 2024, **15**, 2510.