

Supporting info for

Transformations of an FCC catalysts and carbonaceous deposits during repeated reaction-regeneration cycles

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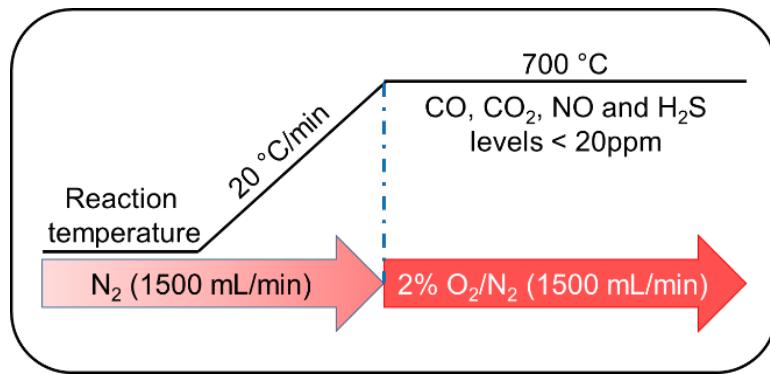


Figure S1: Conditions used during the regeneration of the spent catalyst sample.

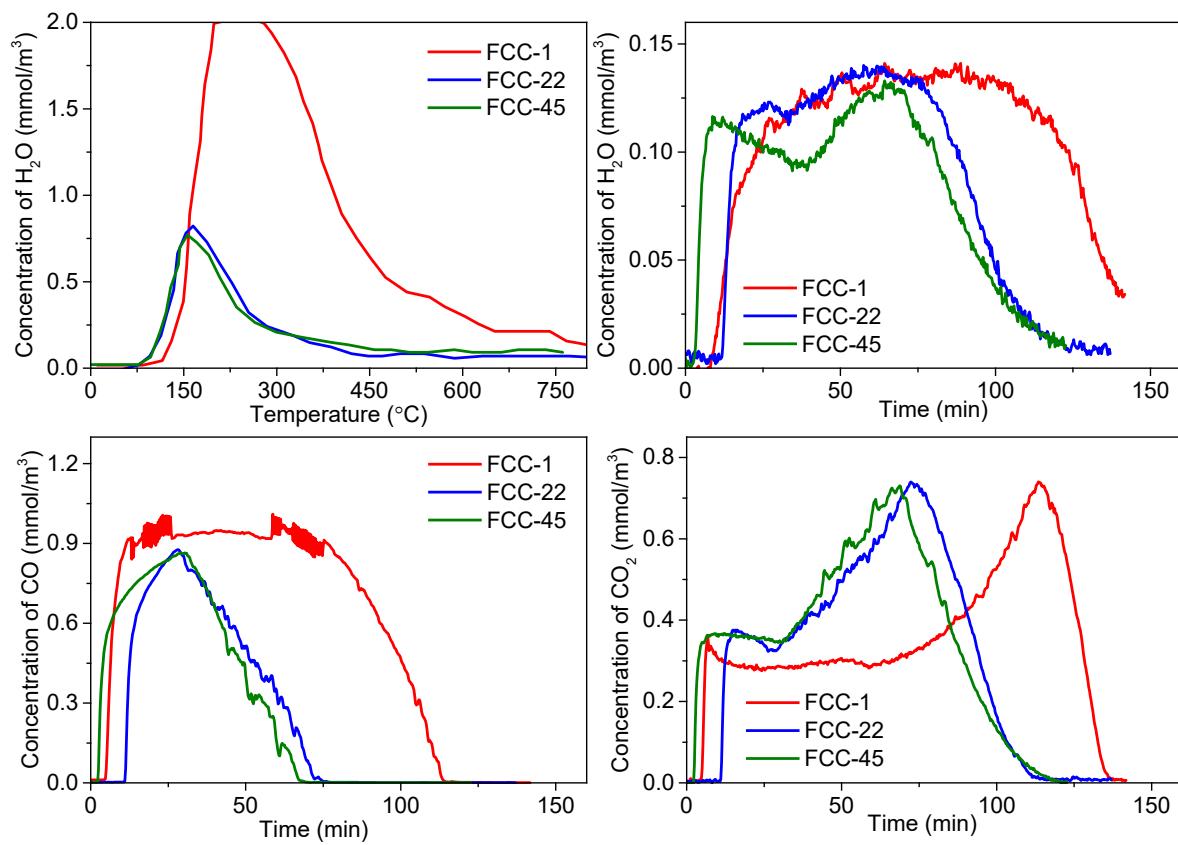


Figure S2: (a) H₂O formation during the treatment step with N₂, (b) H₂O, (c) CO₂ and (d) CO formation profiles during regeneration in 2% O₂/N₂ at 700 °C

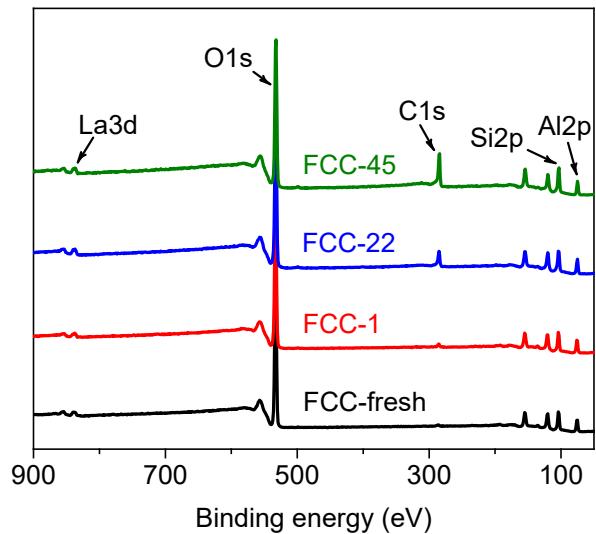


Figure S3: Survey scans for the fresh and coked FCC catalysts, obtained via XPS analysis.

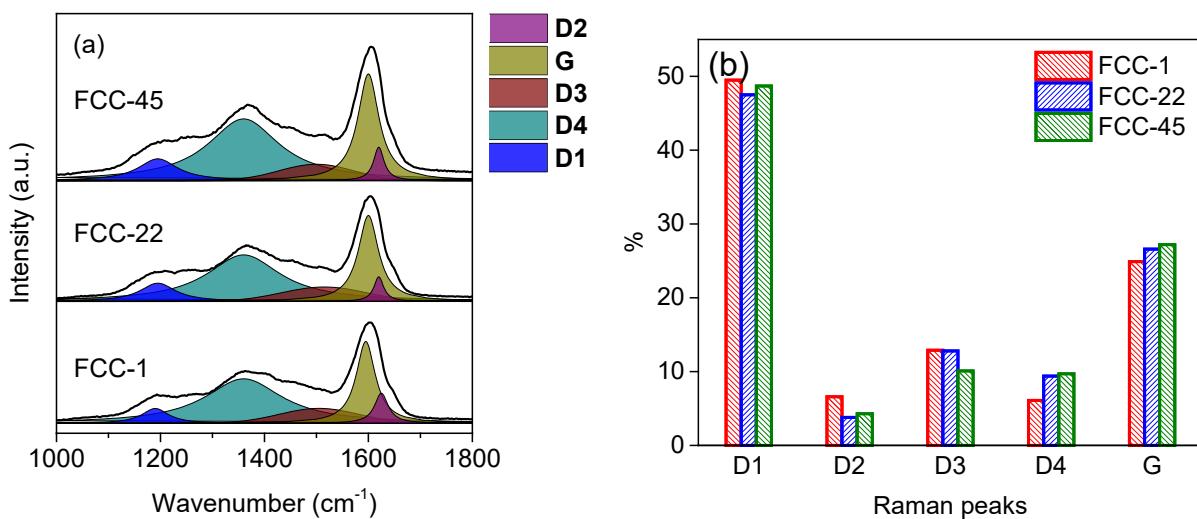


Figure S4: (a) Raman spectra (region 1000 – 1800 cm⁻¹) of the coked catalysts at 30 °C, (b) Results of deconvolution of Raman spectra for FCC-1, 22 and 45.

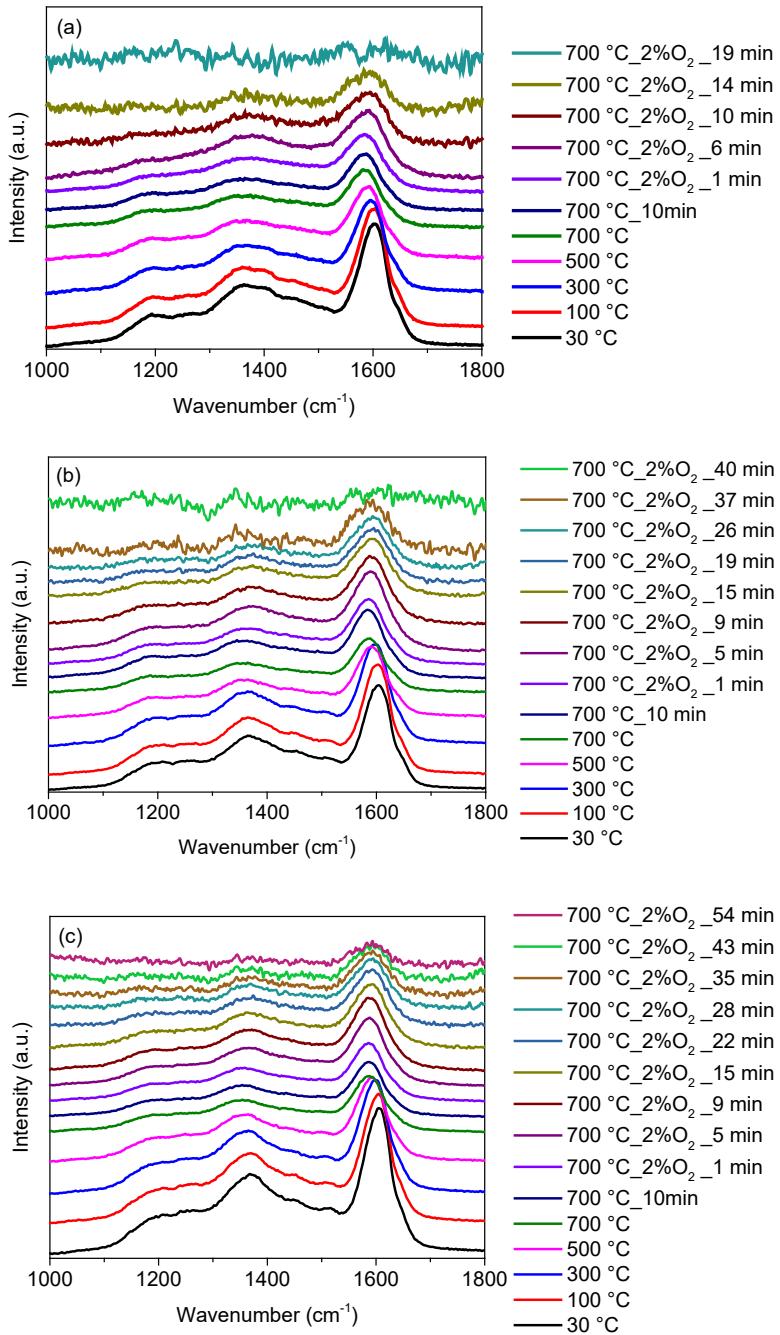


Figure S5: In-situ Raman analysis of (a) FCC-1, (b) FCC-22 and (c) FCC-45. The samples were heated in N₂ from 30 – 700 °C, held at 700 °C for 10 min (in N₂) and regenerated in 2% O₂/N₂ at 700 °C until the Raman signals for coke disappeared.

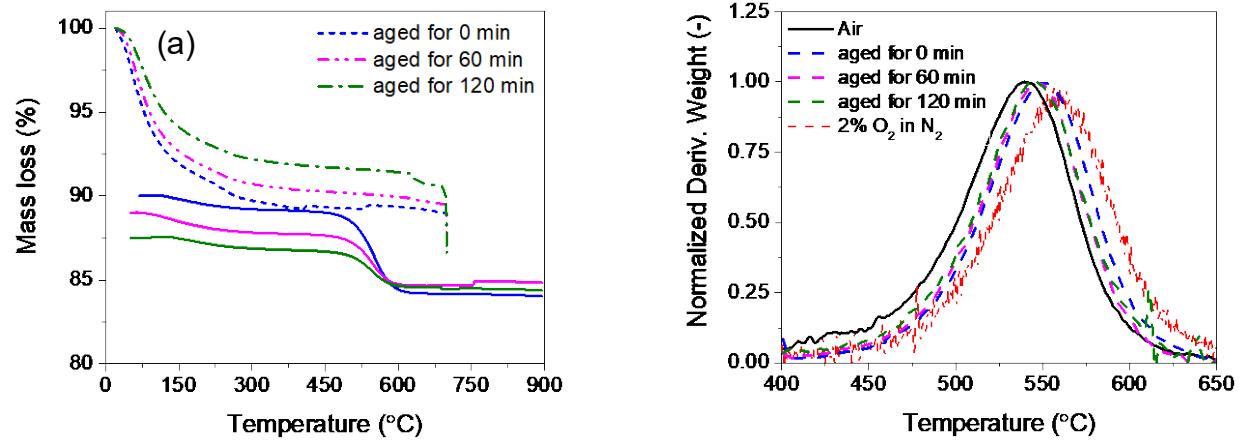


Figure S6: Effect of thermal ageing on the regeneration of FCC-1: (a) Change in mass with temperature during ageing (broken lines) and regeneration (solid lines) and (b) comparison of TPO curves during regeneration. The noise in the data was observed due to external conditions (mainly vibrations and air draughts).

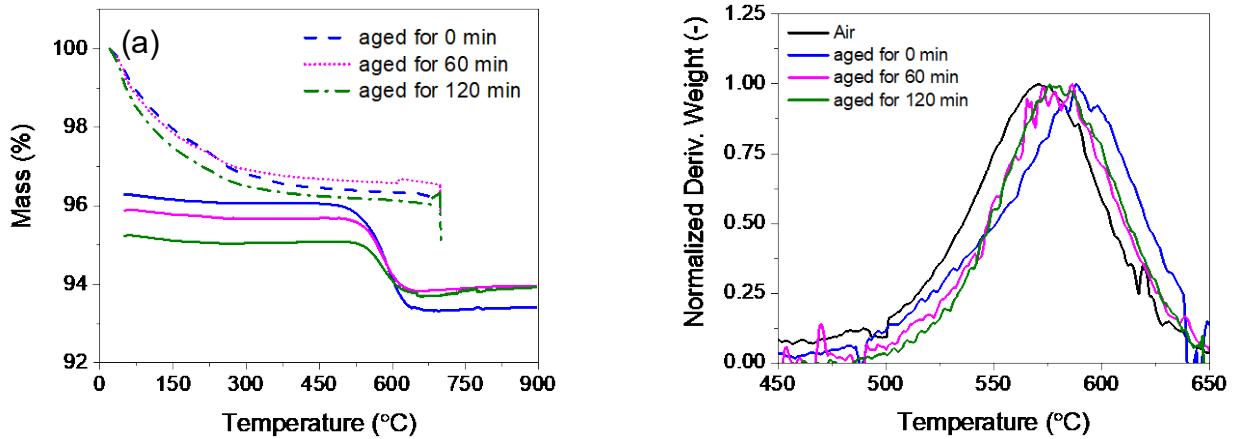


Figure S7: Effect of thermal ageing on the regeneration of FCC-22: (a) Change in mass with temperature during ageing (broken lines) and regeneration (solid lines) and (b) comparison of TPO curves during regeneration. The noise in the data was observed due to external conditions (mainly vibrations and air draughts).

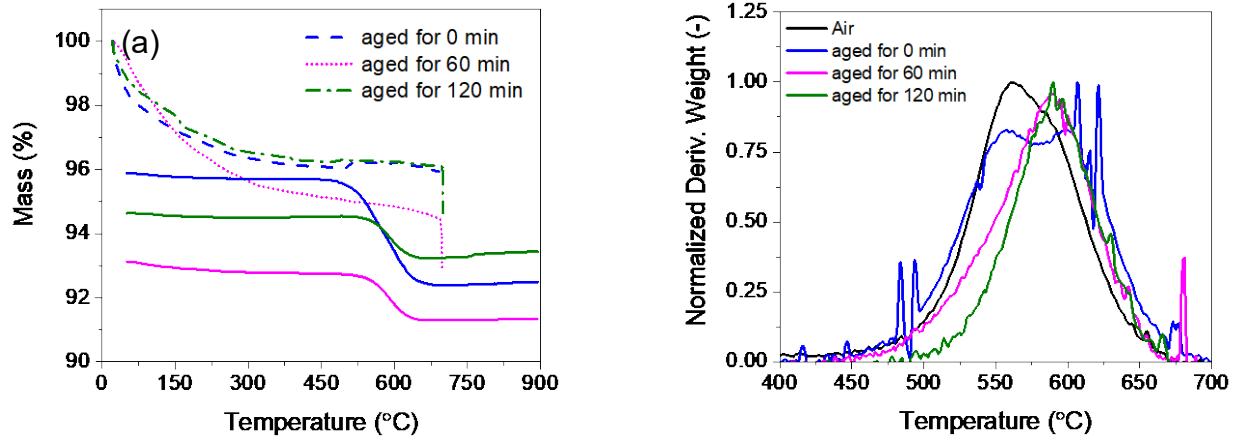


Figure S8: Effect of thermal ageing on the regeneration of FCC-45: (a) Change in mass with temperature during ageing (broken lines) and regeneration (solid lines) and (b) comparison of TPO curves during regeneration. The noise in the data was observed due to external conditions (mainly vibrations and air draughts).

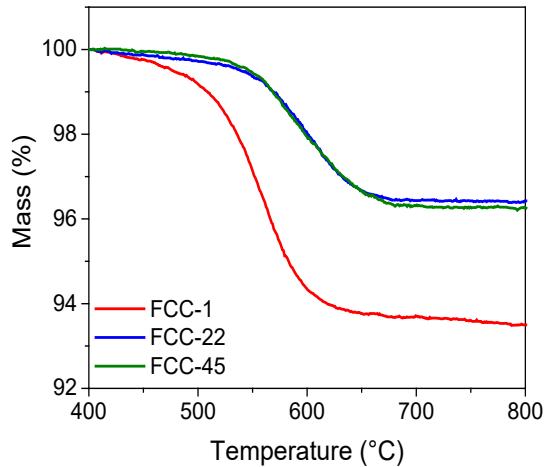


Figure S9: Change in mass w.r.t. temperature for FCC-1, 22 and 45 after DCM extraction.

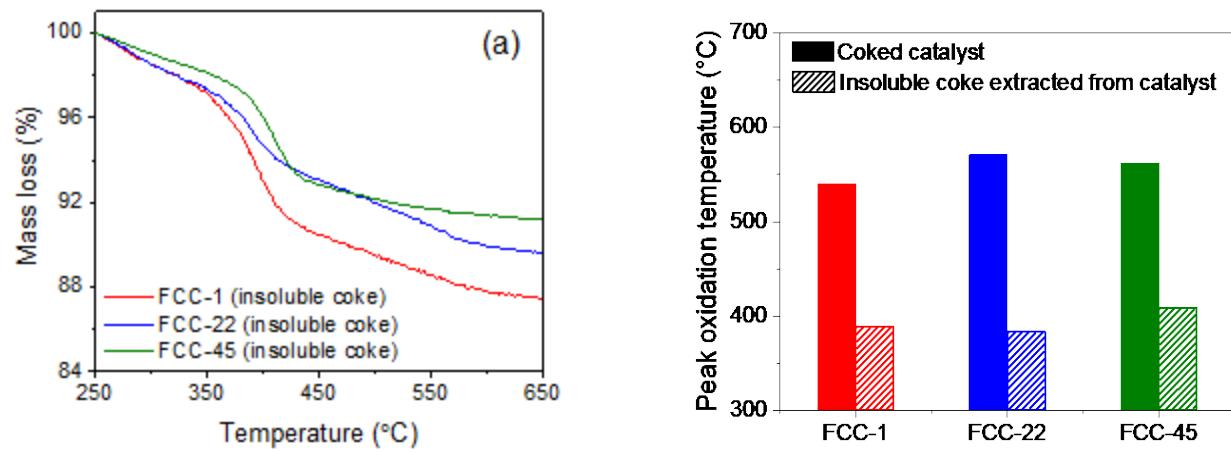


Figure S10: (a) Change in mass w.r.t. temperature and (b) Comparison of peak oxidation temperatures for the coked catalyst and insoluble coke extracted from FCC-1, 22 and 45.

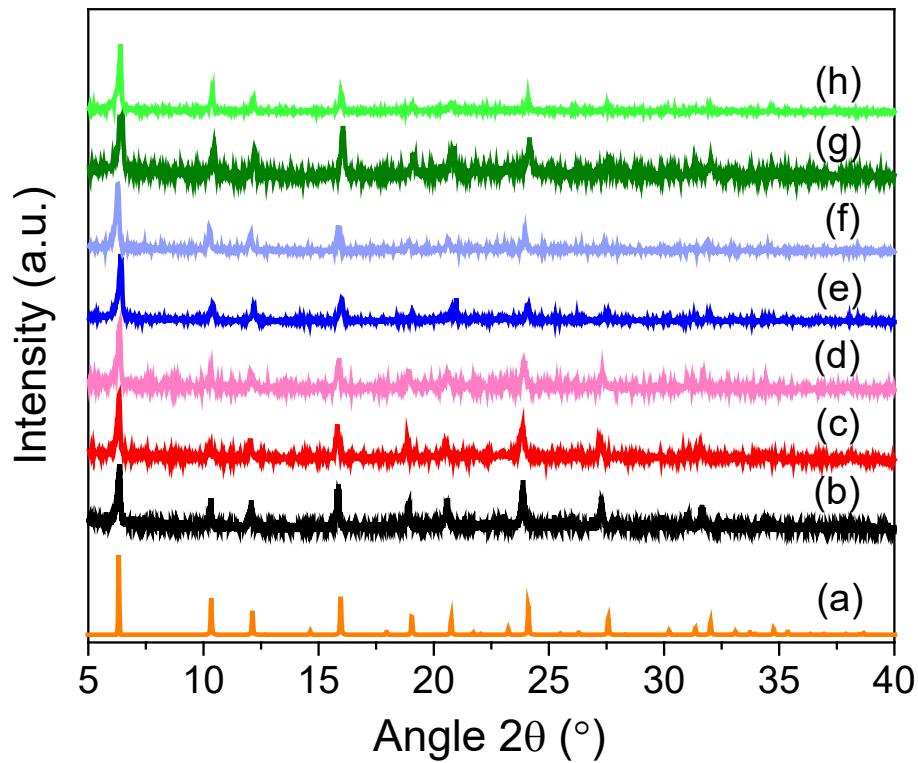
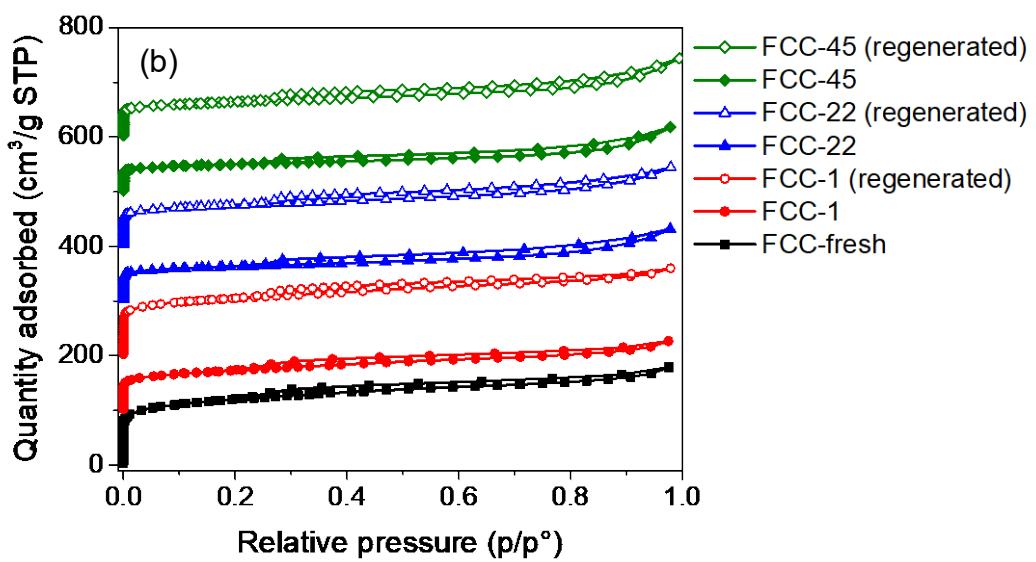
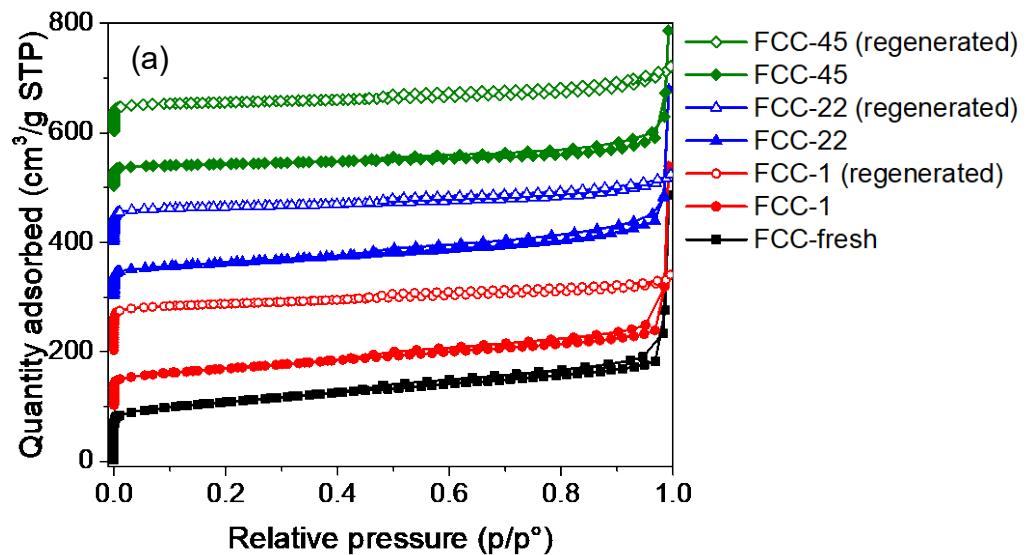


Figure S11: X-ray diffractograms of the fresh, coked and regenerated FCC catalysts. (a) USY, (b) FCC-fresh, (c) FCC-1, (d) FCC-1 (regenerated), (e) FCC-22, (f) FCC-22 (regenerated), (g) FCC-45 and (h) FCC-45 (regenerated).



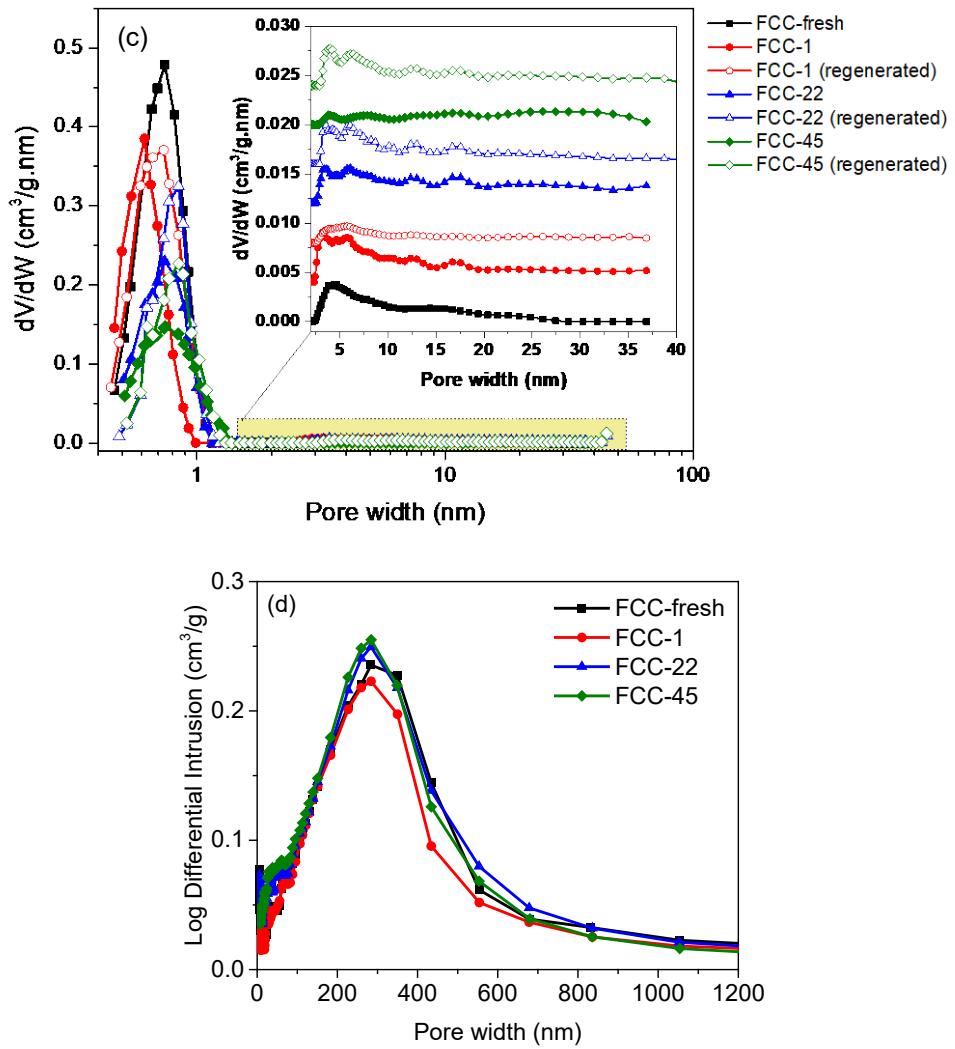


Figure S12: (a) N₂ sorption isotherms, (b) O₂ sorption isotherms, for the fresh, coked and regenerated FCC catalysts, (c) Pore size distribution from N₂ sorption isotherms, with emphasis on the mesopore region (2 - 40 nm) in the inset, and (d) incremental intrusion with respect to pore diameter curves, obtained from mercury intrusion porosimetry. The isotherms in (a) and (b) are offset by 100 cm³/g on the y-axis for clarity. The curves in (c) are offset by 0.004 cm³/g.nm on the y-axis for clarity.

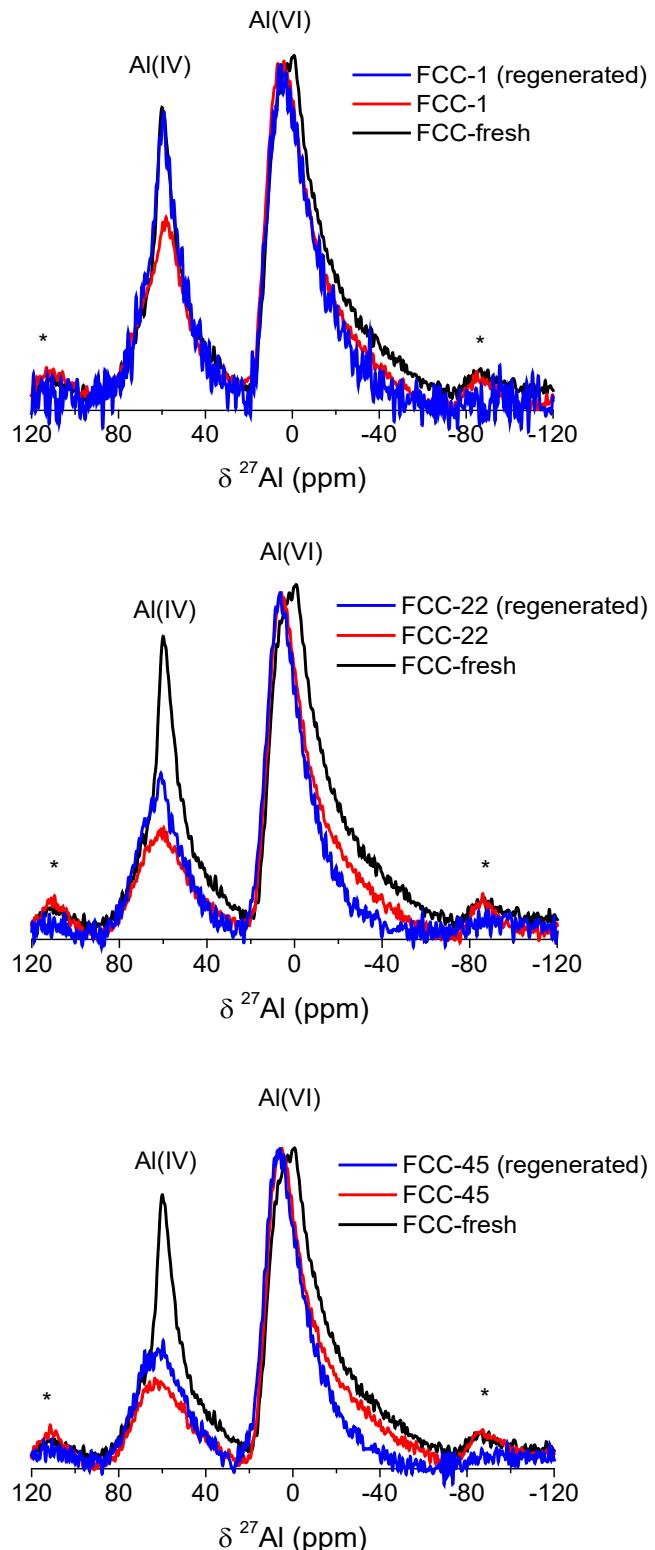


Figure S13: Comparison of FCC-fresh with the coked and regenerated FCC catalysts. (*) spinning sidebands)

Table S1: Quantity of matter (in $\mu\text{mol/g}_{\text{catalyst}}$) of the compounds containing C, H, S and N observed during the N_2 treatment steps and regeneration with 2% O_2/N_2 for coked FCC samples.

Compound	FCC-1		FCC-22		FCC-45	
	N_2	2% O_2/N_2	N_2	2% O_2/N_2	N_2	2% O_2/N_2
CH_4	0.50	0.88	1.23	0.10	0.98	0.06
C_2H_6	0.01	0.00	0.00	0.00	0.00	0.00
C_2H_4	0.01	0.01	0.04	0.00	0.02	0.00
C_3H_8	0.01	0.00	0.03	0.00	0.07	0.00
H_2S	0.34	6.65	0.03	2.45	0.03	2.35
COS	0.01	0.27	0.00	0.04	0.00	0.03
CS_2^*	0.16	5.81	0.03	3.03	0.03	2.09
SO_2	0.29	10.84	0.01	1.87	0.01	1.87
SO_3	0.08	0.21	0.04	0.15	0.06	0.16
HCN	0.04	0.45	0.19	0.43	0.14	0.43
N_2O	0.00	0.08	0.00	0.22	0.00	0.34
NO	0.01	0.89	0.01	1.25	0.00	1.70
NO_2	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	0.01	0.00	0.00	0.00	0.00	0.00

*The analysis of CS_2 is influenced by other compounds, mainly CO_2 . Therefore, the observed values for CS_2 in the atmosphere of this work are not reliable.

Table S2: First-order Raman bands and their vibration modes¹

Peak ID	Raman shift (cm⁻¹)	Fitting Type	Type of Carbon
G	~1580	Lorentz	Ideal graphitic
D1	~1350	Lorentz	Disordered graphitic edges, in-plane imperfections
D2	~1620	Lorentz	Disordered graphitic surface
D3	~1500	Gaussian	Amorphous carbon, sp ² bonded
D4	~1200	Lorentz	Disordered graphitic lattice, ionic impurities

Table S3: Surface area and micropore properties of the aged and regenerated FCC samples. N₂ (or O₂) indicate the gas used for the physisorption analysis.

Catalyst	BET surface area (m ² /g)	Micropore volume (cm ³ /g)	Micropore area (m ² /g)
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Samples thermally aged in N₂ atmosphere for 2 h:

FCC-1_N ₂ _aged at 700 °C	228	0.09	160
FCC-22_N ₂ _aged at 700 °C	210	0.09	142
FCC-45_N ₂ _aged at 700 °C	146	0.08	123

Regenerated samples (500 °C or 750 °C indicates the regeneration temperature):

FCC-1_N ₂ _500 °C	302	0.095	201
FCC-22_N ₂ _500 °C	220	0.069	147
FCC-45_N ₂ _500 °C	188	0.056	119
FCC-1_N ₂ _750 °C	298	0.140	208
FCC-22_N ₂ _750 °C	216	0.110	156
FCC-45_N ₂ _750 °C	189	0.080	133
FCC-1_O ₂ _500 °C	320	0.076	203
FCC-22_O ₂ _500 °C	223	0.055	145
FCC-45_O ₂ _500 °C	188	0.044	118
FCC-1_O ₂ _750 °C	314	0.075	202
FCC-22_O ₂ _750 °C	226	0.054	145
FCC-45_O ₂ _750 °C	192	0.045	120

Table S4: Crystallite sizes for the fresh and coked FCC catalysts (determined using Scherrer equation,² at $\theta = 6.18$, corresponding to the plane 111)

$$\text{Crystallite size} = \frac{K\lambda}{\beta \cos\theta}$$

where:

- K is a dimensionless shape factor (here K = 0.94);
- λ is the X-ray wavelength;
- β is the line broadening at half the maximum intensity (FWHM), in radians;
- θ is the Bragg angle.

Catalyst	Crystallite size (nm)
FCC-fresh	42.7
FCC-1	40.5
FCC-1 (regenerated)	41.2
FCC-22	38.6
FCC-22 (regenerated)	38.9
FCC-45	34.6
FCC-45 (regenerated)	35.1

Table S5: Combined meso- and macropore volume, obtained from mercury porosimetry.

Catalyst	Meso- and macropore volume (cm ³ /g)
FCC-fresh	1.88
FCC-1	1.85
FCC-22	1.91
FCC-45	1.92

References

1. A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl, *Carbon*, 2005, **43**, 1731-1742.
2. B. D. Cullity and S. R. Stock, *Elements of X-Ray Diffraction*, Prentice-Hall Inc., 3 edn., 2001.