Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Understanding catalyst deactivation during the direct cracking of crude oil

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Calculations for catalytic performance and coke analysis:

Catalytic cracking of AL performance:

Total flow rate: $= \frac{F_{He}}{\%V_{He}} \times 100\ ml \cdot min^{-1}$ (Equation S*1*)

Flow rate of internal standard He: $F_{He}\ ml \cdot min^{-1}$

Percentage of gas volume: $\%V_x$

Flow of each component $F_x\ = \frac{Total\ flow \times \%V_x}{100} \times 100\ ml \cdot min^{-1}$ (Equation S*2*)

Mass flow of each component $M_x\ = \frac{F_x \times MW_x}{R \times T}\ g \cdot min^{-1}$ (Equation S*3*)

Molecular weight of each component $= MW_\mathrm{x}\ g \cdot mol^{-1}$

R is the gas constant and T is temperature in Kelvin

$yield\ wt.\%\ = \frac{M_x}{mass\ flow\ of\ AL\ (g.min^{-1})} \times 100$ (Equation S*4*)

Thermo-gravimetric analysis (TGA):

Hard coke and coke precursors are defined as following equation related to Figure S1

Coke precursors (wt.%) $= \frac{m_0 - m_e}{m_z} \times 100$ (Equation S*5*)

Hard coke (wt.%) $= \frac{m_e - m_z}{m_z} \times 100$ (Equation S*6*)

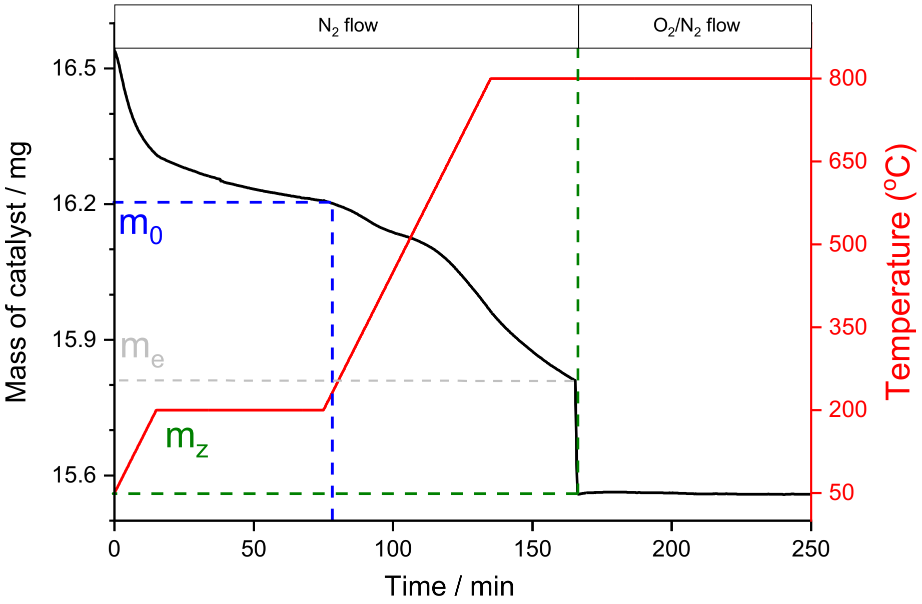

Figure. S1: Coke quantification method by thermo-gravimetric analysis. TGA of spent catalysts in MZFBR after catalytic cracking.

Calculations for determination of aluminium content (molar fraction) in zeolite framework and levels of dealumination using unit cell size (UCS) parameters derived from powder X-ray diffraction data:

The quantitative evaluation of the migration of aluminum from the framework during thermal, hydrothermal treatment and after being acted in the cracking process can be achieved by linking a unique unit cell size (UCS) parameter with the effective framework composition.[58] The unit cell parameters of a zeolite are directly correlated with the framework composition. As such, increasing the content of aluminum atoms in the frameworks induces an expansion of the UCS parameters because of relative longer tetrahedral Al-O bonds (~ 1.74 Å) compared to Si-O (~ 1.63 Å) ones. Thus, the UCS parameter well represents a "framework" tetrahedral aluminum centers associated with Brønsted acidity and can be derived from acidity evaluation applying NH_3 chemisorption at high temperature region (below 300 °C). Therefore, the framework aluminum mole fraction (x_{Al})[58,59] can be derived through calculations involving:

$$Stoichiometric\ acidity\ [mol \cdot g^{-1}] = \frac{1}{M_w^{zeolite}} \qquad \text{(Equation S}7\text{)}$$

$$M_w^{zeolite} = M_w^{SiO_2} \cdot SAR + M_w^{Al_2O_3} + A_r^H \qquad \text{(Equation S}8\text{)}$$

where stoichiometric acidity is strong acidity population, Brønsted acidity, ($\mathrm{mol \cdot g^{-1}}$) determined from NH_3 chemisorption; $M_w^{zeolite}$ - molecular weight of zeolite with the formula $(SiO_2)_{SAR}(Al_2O_3)H$ where SAR represents framework SiO_2:Al_2O_3 molar ratio; M_w^{SiO2}, M_w^{Al2O3} and A_r^H are molecular weights of SiO_2, Al_2O_3 and atomic weight of hydrogen, respectively. Derived SAR value can be transformed to aluminum mole fraction (x_{Al}) to express aluminum content in the framework by using Equation S9:

$$x_{Al} = \frac{[Al]}{[Al]+[Si]} = \frac{1}{1+SAR/2} \qquad \text{(Equation S}9\text{)}$$

The extend of dealumination and framework aluminum content can be estimated applying Equation S10:

$$V_x = V_{Si} - V_{Si} \cdot \left(1 - \left(\frac{d_{Al-O}}{d_{Si-O}}\right)^3\right) \cdot x_{Al} \qquad \text{(Equation S}10\text{)}$$

where V_x is experimentally determined unit cell volume of the framework with x_{Al} mole fraction and V_{Si} is unit cell volume of purely siliceous zeolite framework. Considering the tetrahedral Al-O and Si-O bond length (~ 1.74 Å and ~ 1.63 Å, respectively), the Equation S10 transforms to:

$$V_x = V_{Si} \cdot (1 - (1 - 1.2842) \cdot x_{Al}) = V_{Si} \cdot (1 + 0.2842 \cdot x_{Al}) \qquad \text{(Equation S}\mathit{11}\text{)}$$

V_{Si} for purely siliceous zeolite FAU and MFI can be calculated employing the Vx of the zeolite with known framework x_{Al}. The data for H-FAU/30 and H-ZSM-5/23 used in the present study for UCS- x_{Al} correlation are detailed in Table S1.

Table S1. Acidity analysis (based on NH_3 physisorption) of individual zeolite components in ACM-101 formulation

Zeolite	**SAR**	**T_{peak} / °C**		**Acidity / mmol·g^{-1}**			**V_{Si} / $Å^3$**	**Framework**	
		Weak	**Strong**	**Weak**	**Strong**	**Total**		**x_{Al} /-**	**Si:Al**
H-FAU/30	30	110	328	0.66	0.42	1.08	14204	0.050	19
H-ZSM-5/23	23	124	402	1.69	0.57	2.26	5331	0.062	15

SAR - SiO_2:Al_2O_3 mole ratio

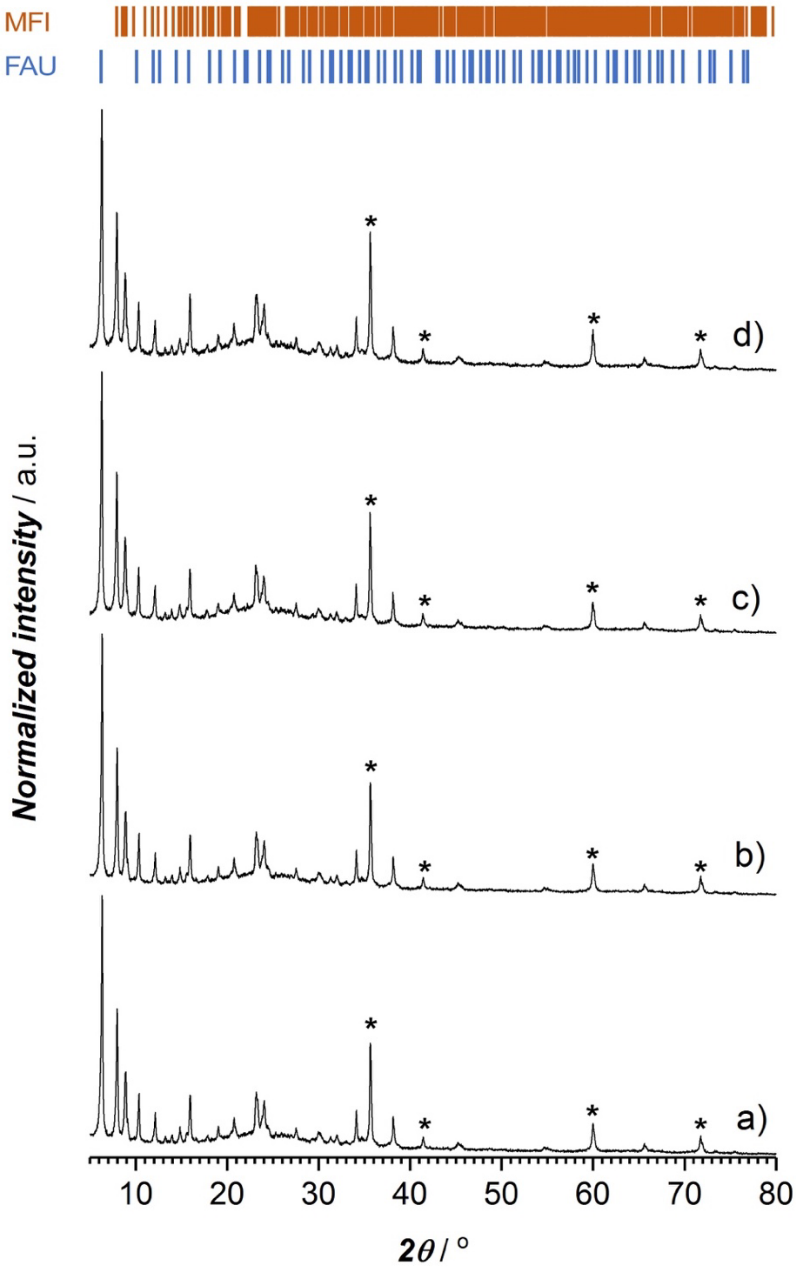

Figure S2. X-ray diffraction patterns of ACM-101 catalyst after calcination (a), steaming (b) and metal deposition steps, ACM-101-M-200 (c) and ACM-101-M-400 (d). Above on the graph expected reflection positions for FAU and MFI zeolite topologies. * marks diffractions attributed to cubic SiC.

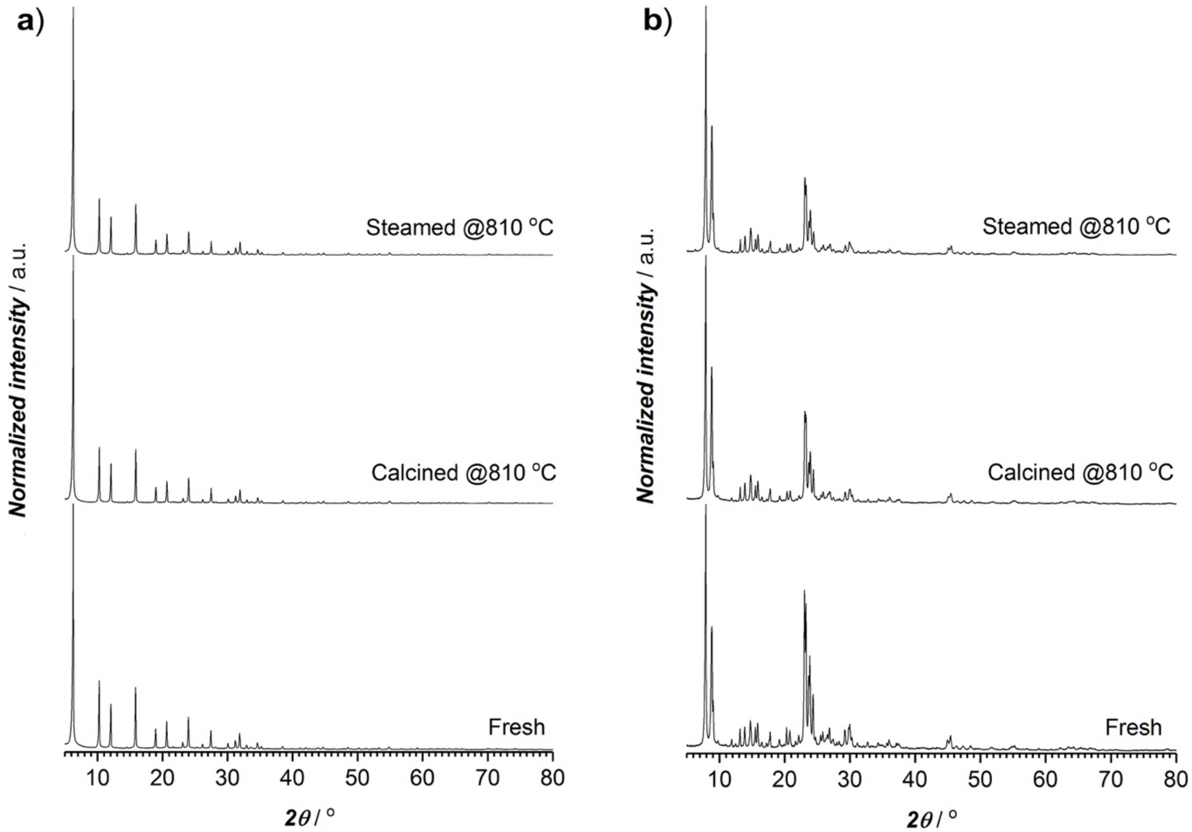

Figure S3. X-ray diffraction patterns of FAU/30 (a) and ZSM-5/23 (b) zeolites fresh, after calcination and steaming.

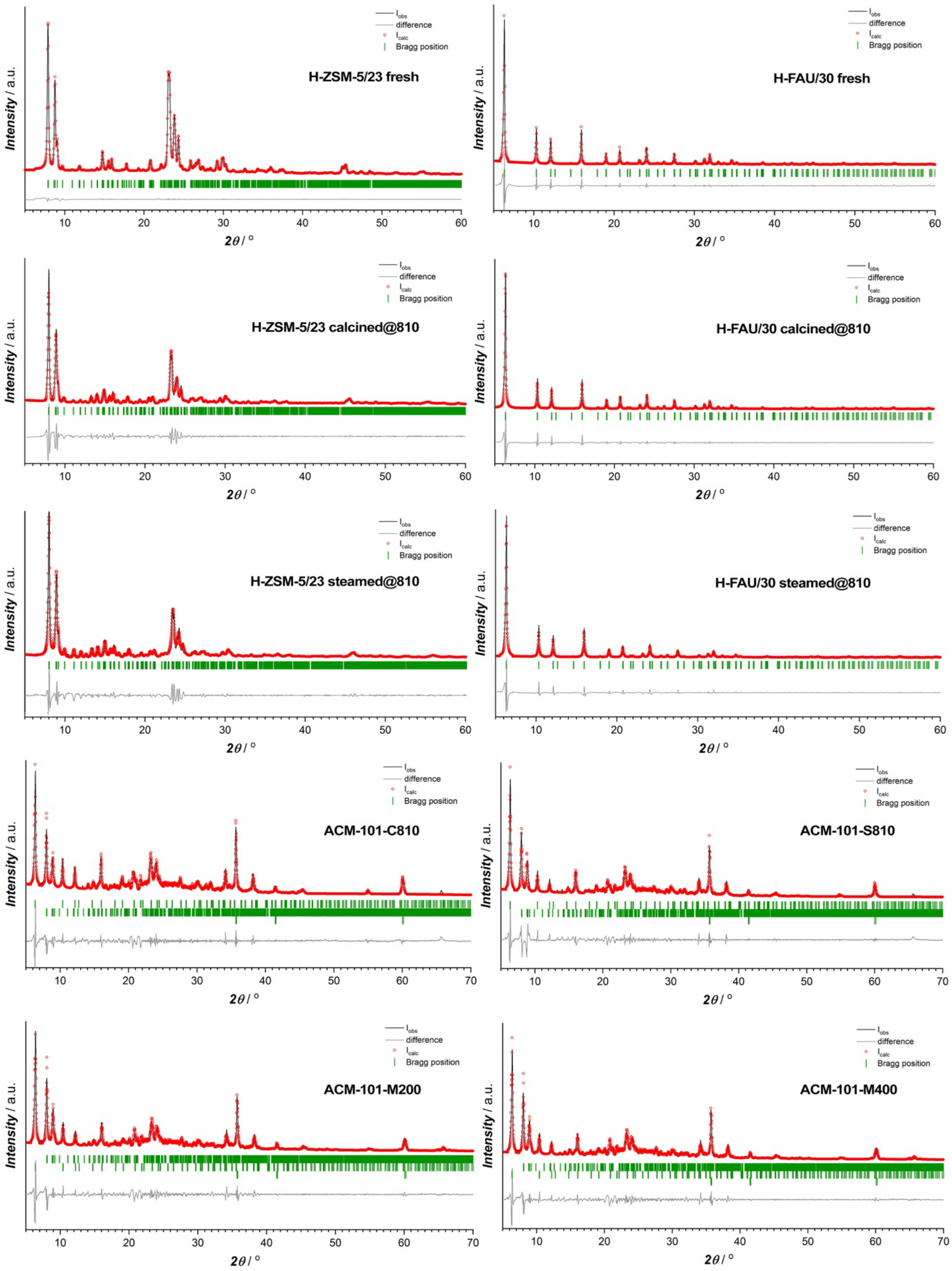

Figure S4. Pawley refinement plots for H-ZSM-5/23, H-FAU/30 fresh and ACM-101 after calcination and steaming treatments together with the same but after poison deposition steps.

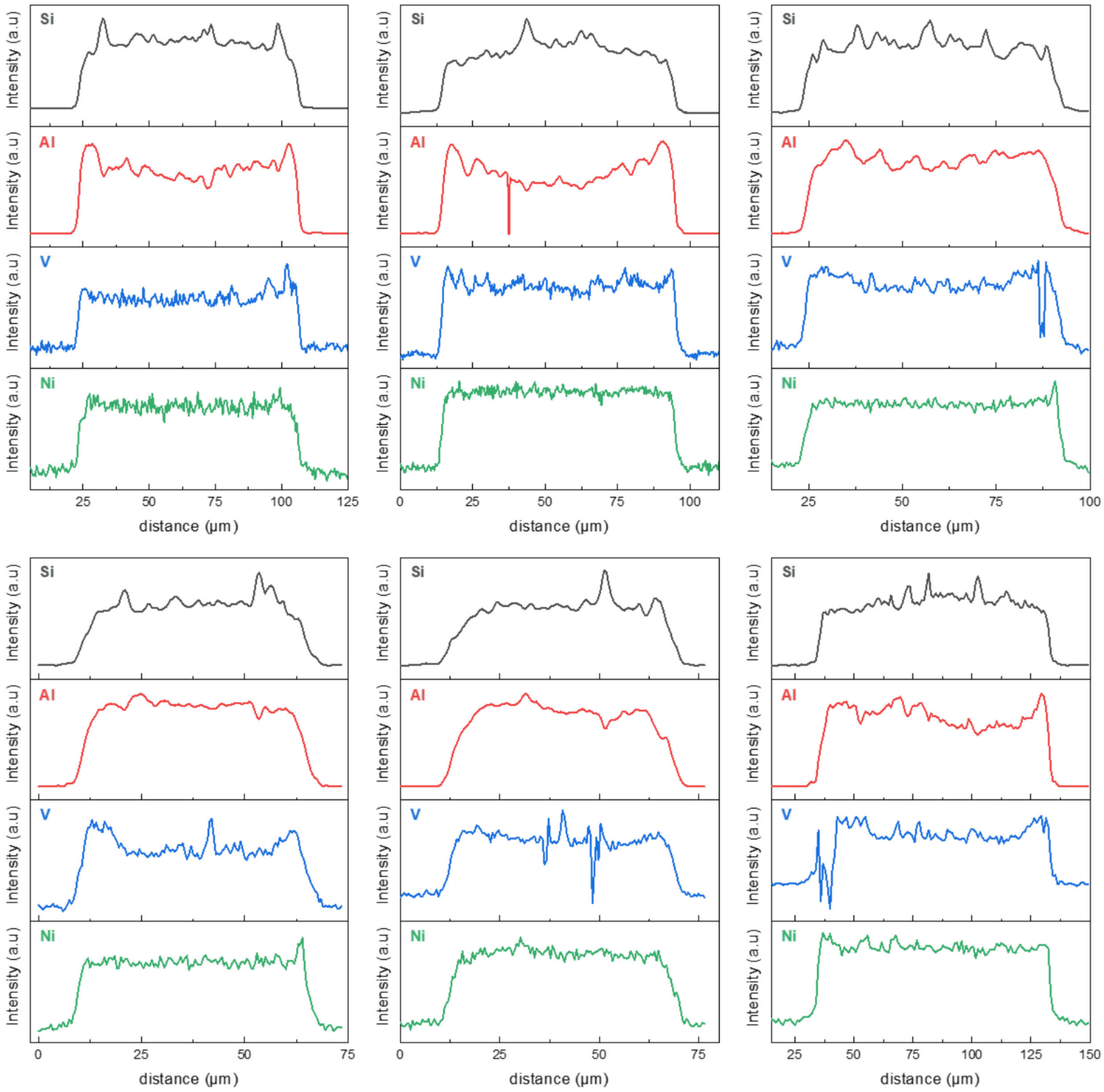

Figure S5. One dimensional analysis of the variation of X-ray intensities from Kα fluorescence lines of Si, Al, V, and Ni elements across particle diameters.

Numerical data for distillation curves for Arabian light and liquid product after the catalytic cracking reaction:

Table S2. Distillation temperature of the Arabian Light crude and the liquid products after the catalytic cracking reaction at different mass recovery.

Product	Boiling Point / °C					
	5 wt.%	10 wt.%	30 wt.%	60 wt.%	80 wt.%	90 wt.%
Arabian Light	69	116	232	391	521	614
ACM-101-C800	131	152	205	277	360	430
ACM-101-S800	50	144	198	266	337	401
ACM-101-M200	187	244	198	266	336	397
ACM-101-M400	126	151	197	265	335	398

Table S3. Chemical composition of the Arabian Light crude and the liquid products after the catalytic cracking reaction.

Product	n-Paraffins / %	iso-Paraffins / %	Naphthenes / %	Aromatics / %
Arabian Light	47.6	28.1	17.6	6.8
ACM-101-C800	19.6	12.5	13.6	54.3
ACM-101-S800	22.8	16.8	15.3	45.1
ACM-101-M200	25.0	18.2	16.1	40.8
ACM-101-M400	23.7	15.5	17.8	43.0