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INSIGHTS INTO THE DEVELOPMENT OF GREENER HIERARCHICAL ZEOLITES APPLIED TO THE HYDROCRACKING OF PLASTIC WASTE

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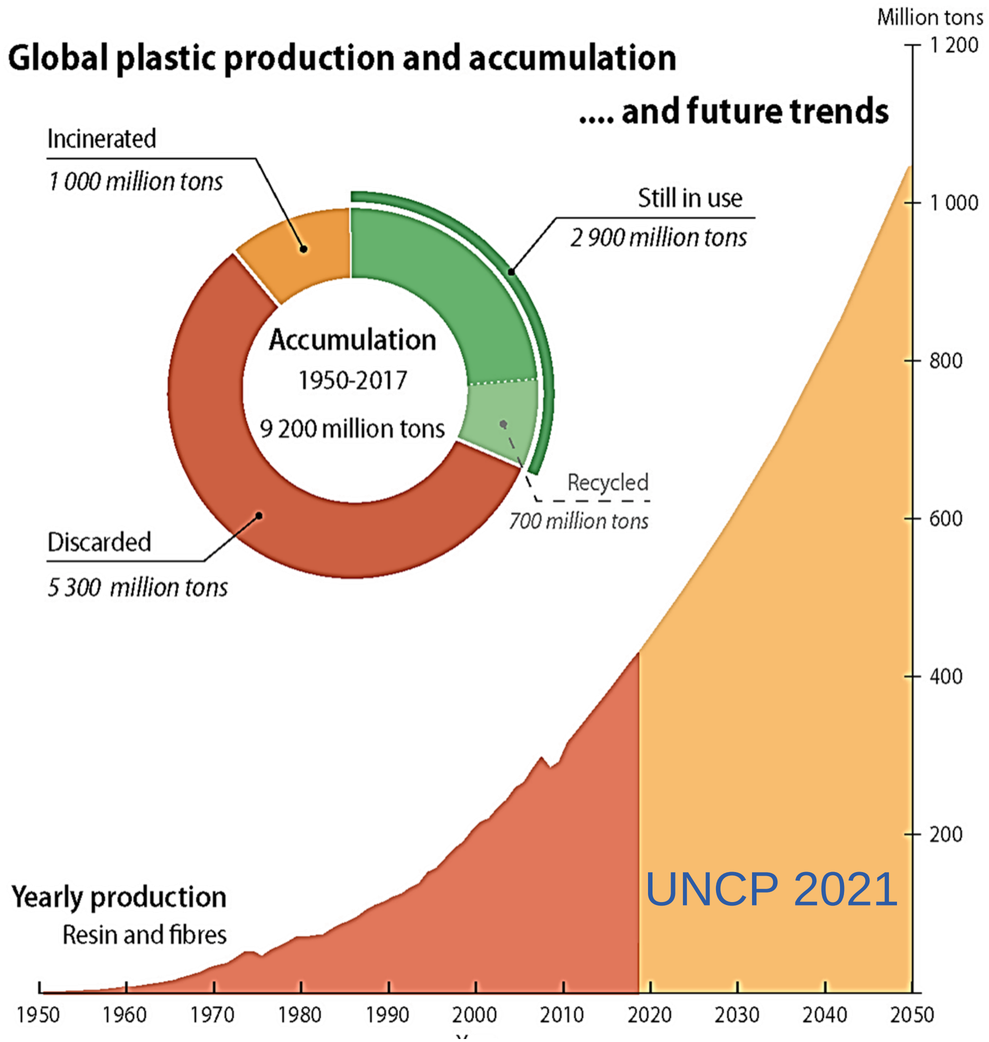
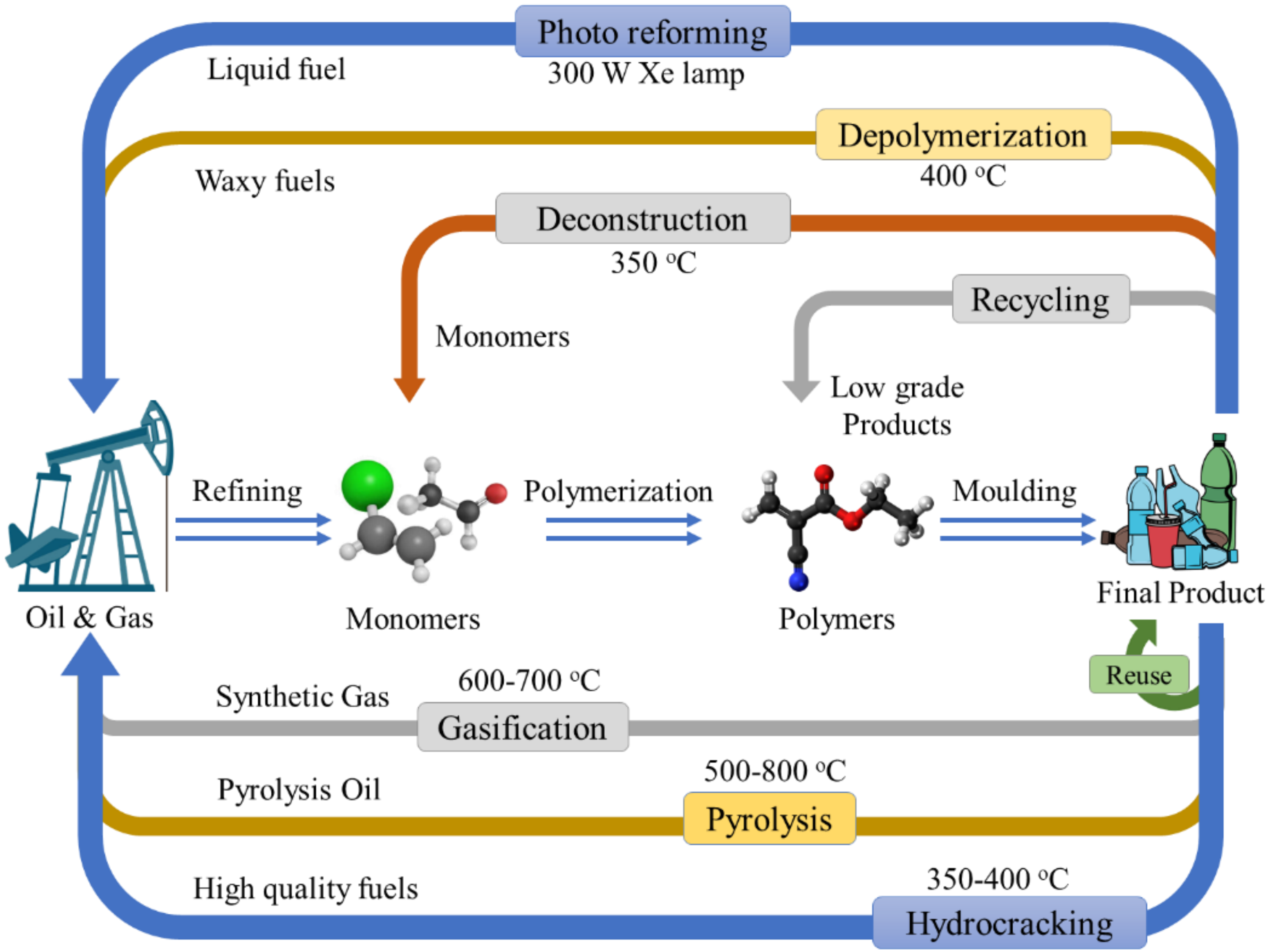
Redefining Waste: Innovative Paths in Recycling



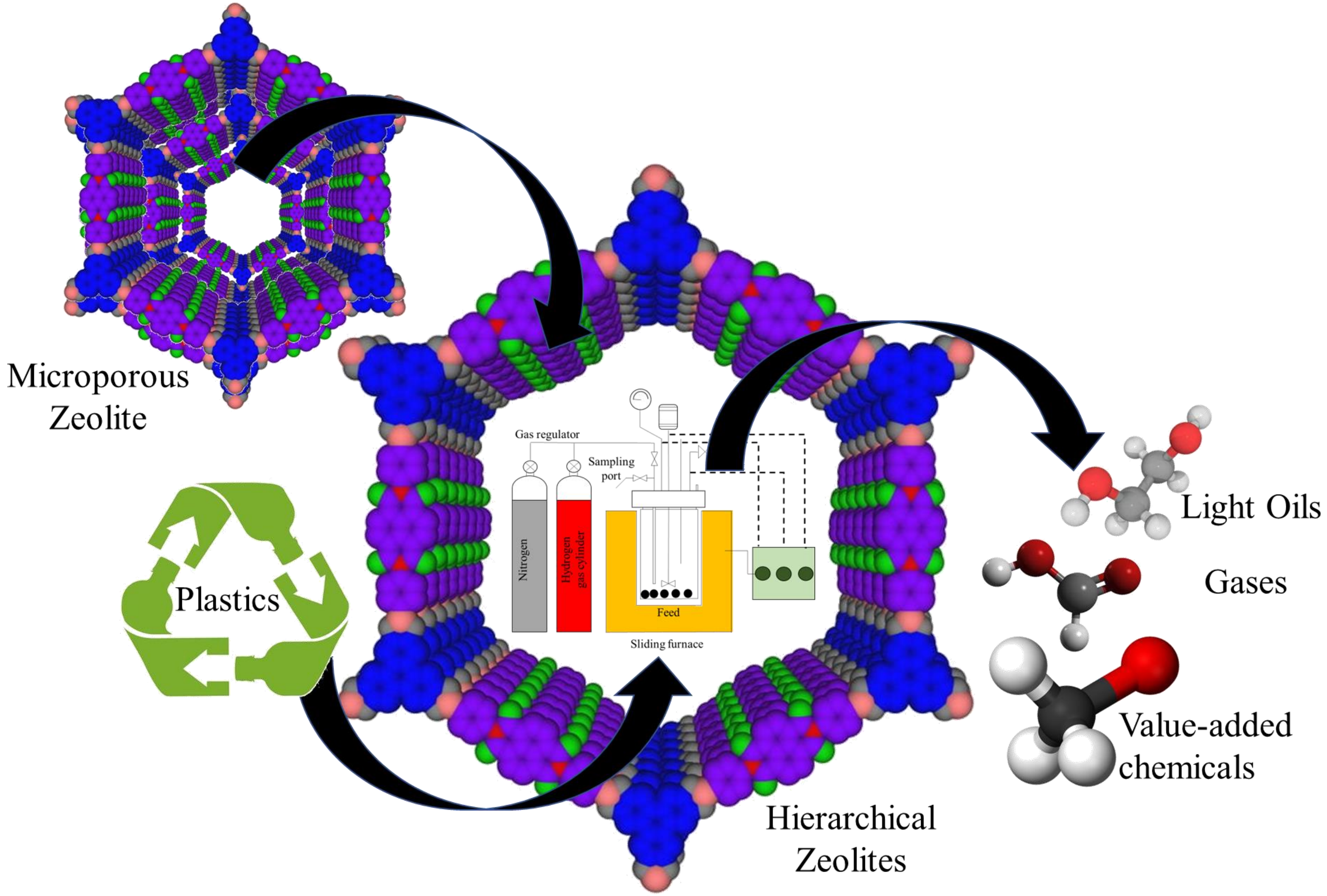


Life Cycle Impact Assessment

Impact category	Unit	Pyrolysis	Hydrocracking
Abiotic depletion	kg Sb eq	1.7×10^{-4}	1.43×10^{-4}
Abiotic depletion (fossil fuels)	MJ	2.99×10^{4}	2.45×10^{4}
Global warming (GWP100a)	kg CO_2 eq	2.56×10^{3}	1.05×10^{3}
Ozone layer depletion (ODP)	kg CFC-11 eq	-4.4×10^{-4}	-2.3×10^{-4}

Azam et al., 2022

Hierarchical Based Zeolites

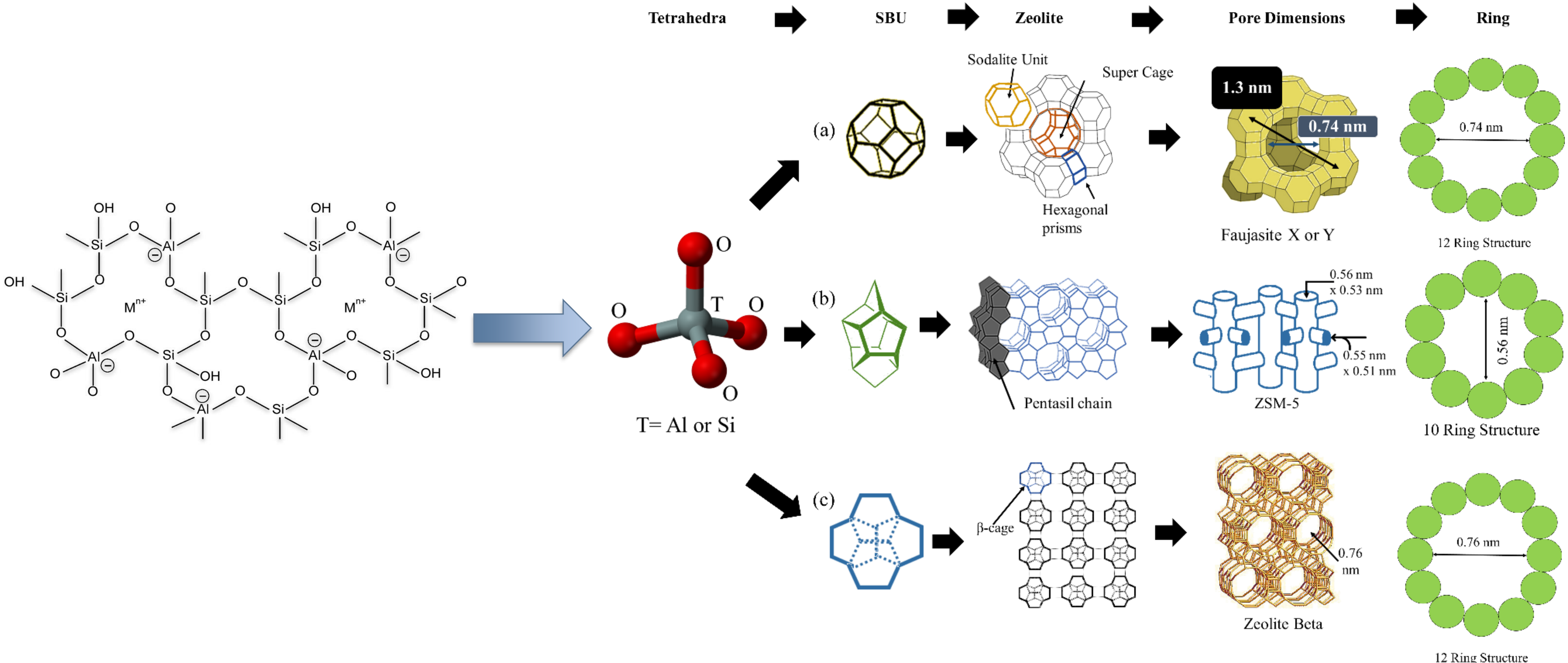


Hieratical Zeolites

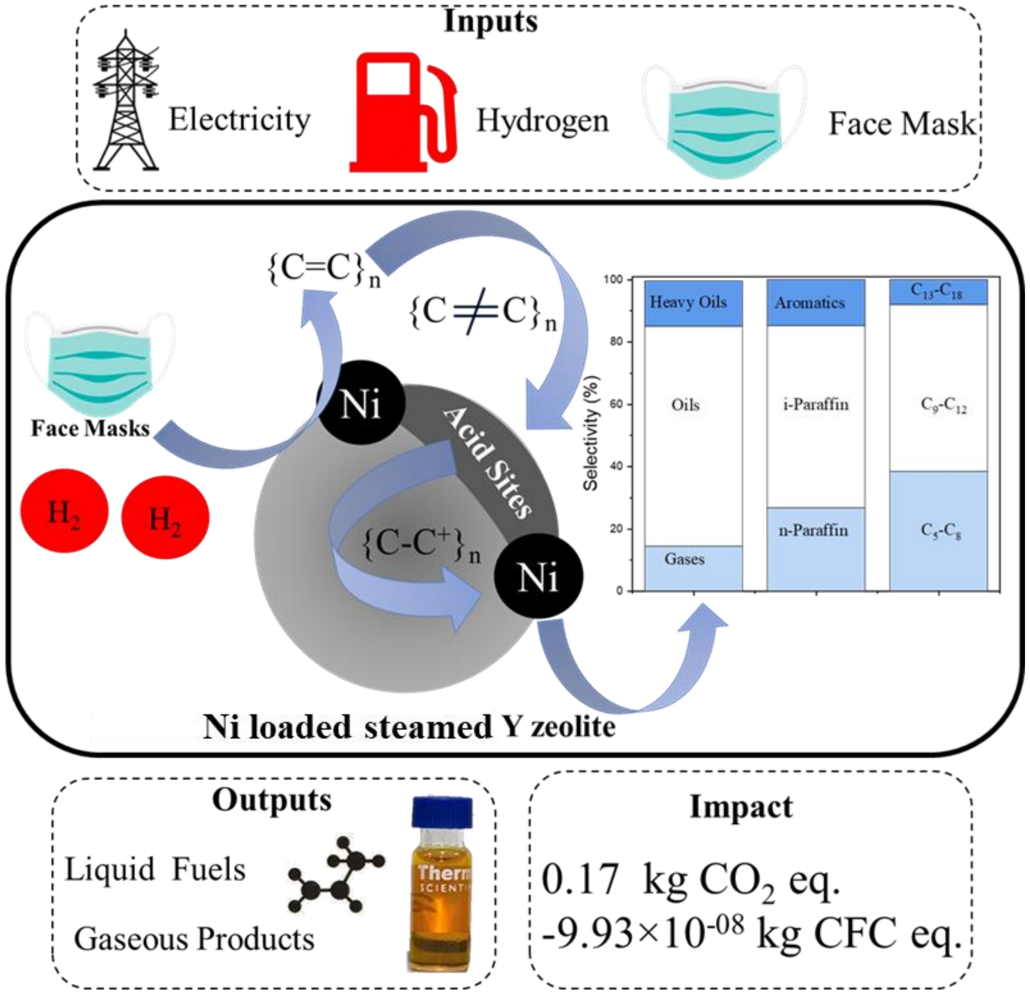
Bottom-up Strategy
- Soft Templating
- Hard Templating

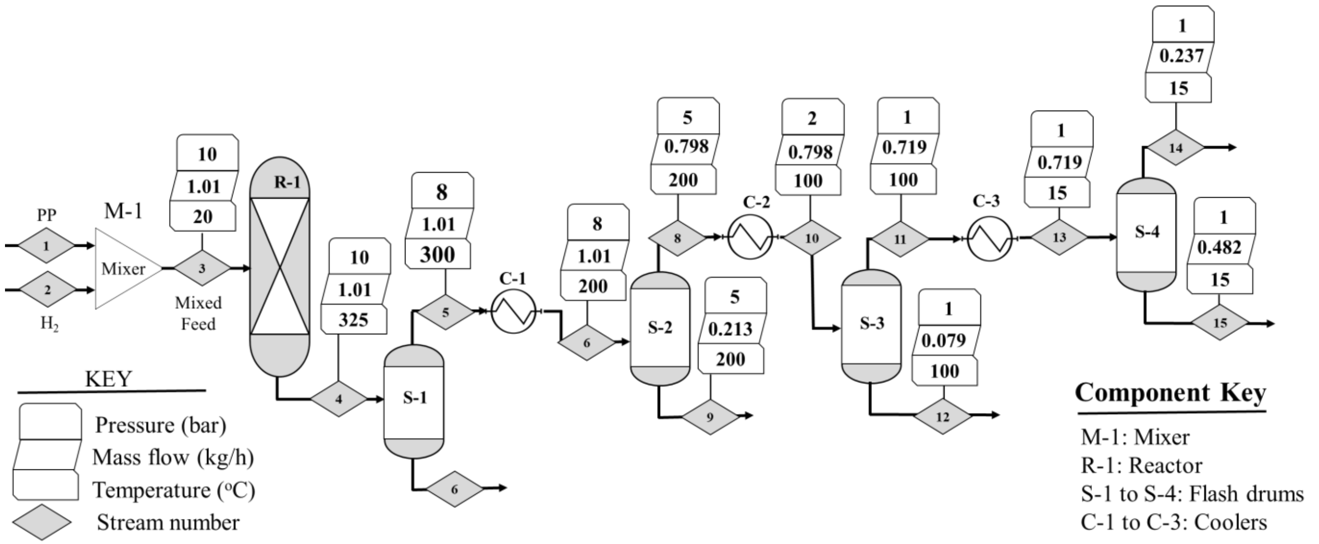
Top-Down Strategy
- Desilication
- Dealumination

Different Zeolite Supports



Hydrocracking of Waste Surgical Masks

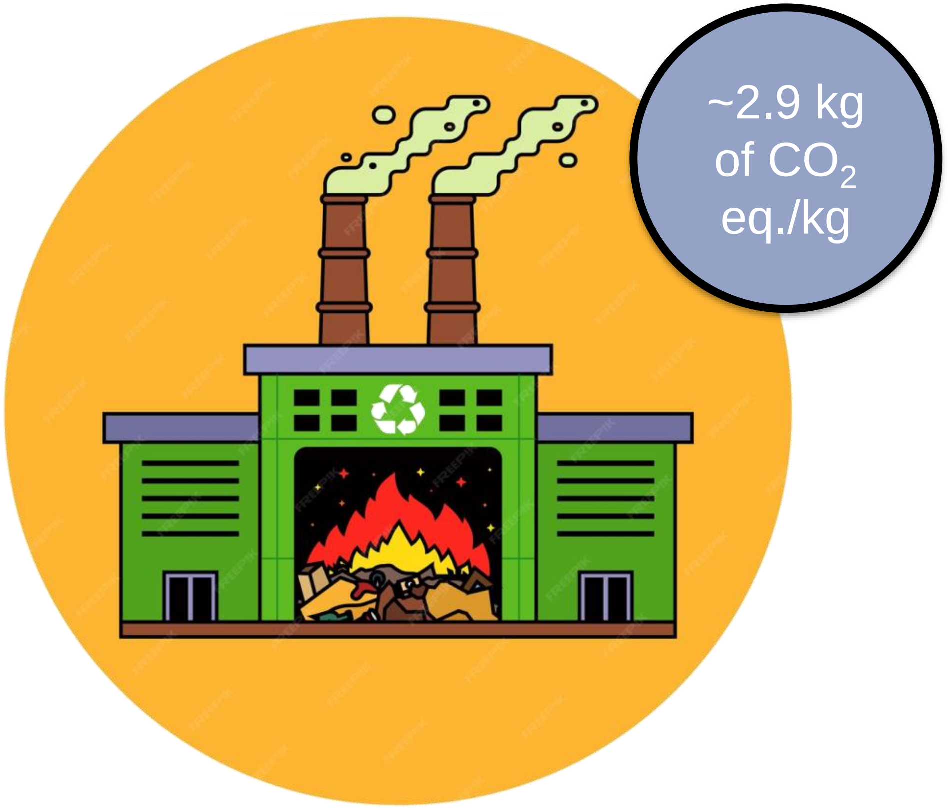




Impact category	Unit	Incineration	Pyrolysis	Hydrocracking
Abiotic depletion	kg Sb eq	2.65×10^{-07}	-6.4×10^{-08}	-8.4×10^{-08}
Abiotic depletion (fossil fuels)	MJ	71.99	49.83	48.77
Global warming (GWP100a)	kg CO_2 eq	4.42	0.39	0.17
Ozone layer depletion (ODP)	kg CFC-11 eq	1.65×10^{-08}	-9×10^{-08}	-9.93×10^{-08}
Marine aquatic ecotoxicity	kg 1,4-DB eq	453.41	-1732.38	-1913.49
Terrestrial ecotoxicity	kg 1,4-DB eq	3.69×10^{-4}	-1.72×10^{-3}	-1.88×10^{-3}

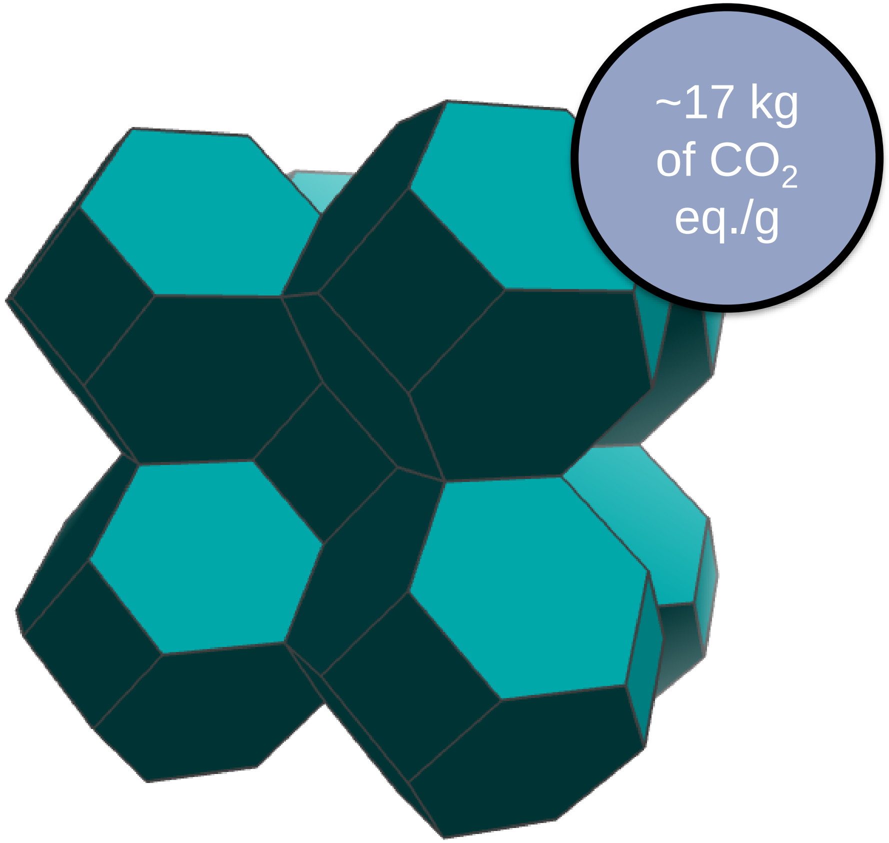
Azam et al., 2023

A Road Towards Sustainable Catalysis



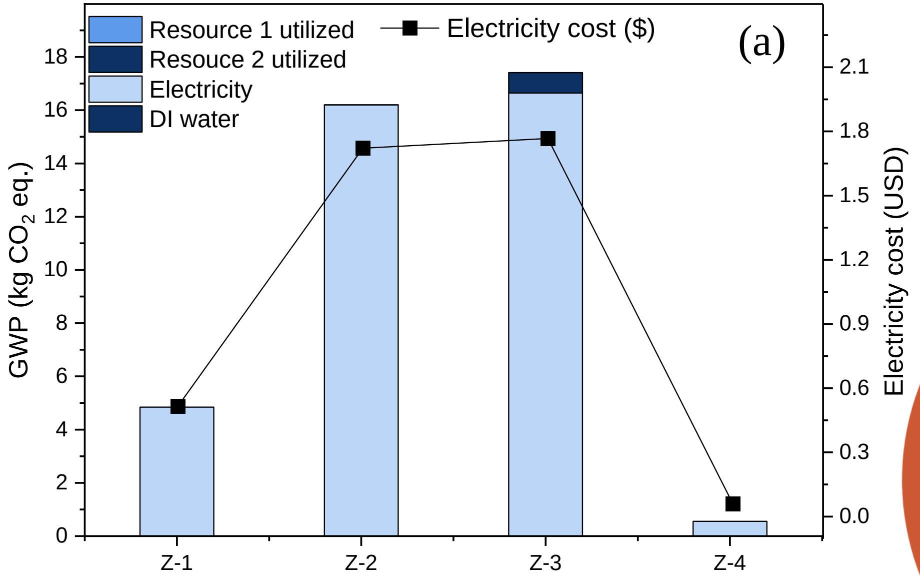
Incineration of plastics

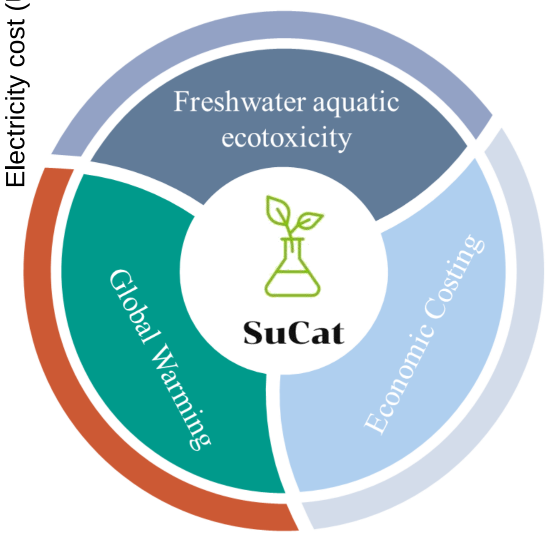
VS

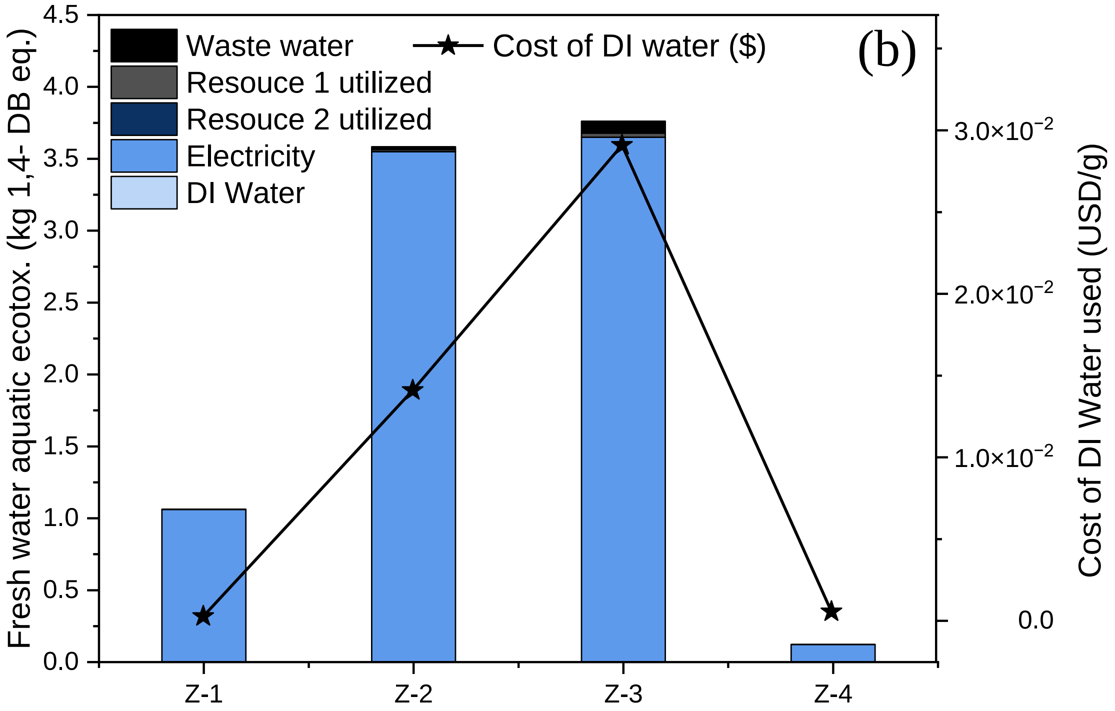


Catalyst Synthesis

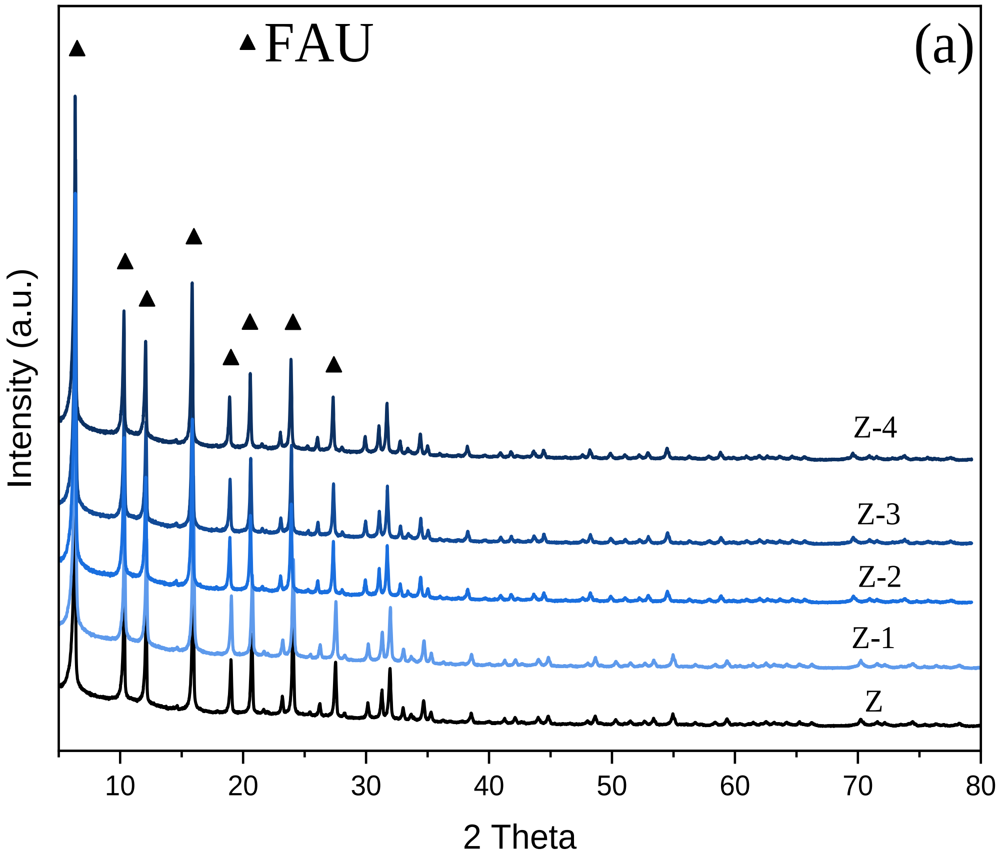
Sustainable Catalysis

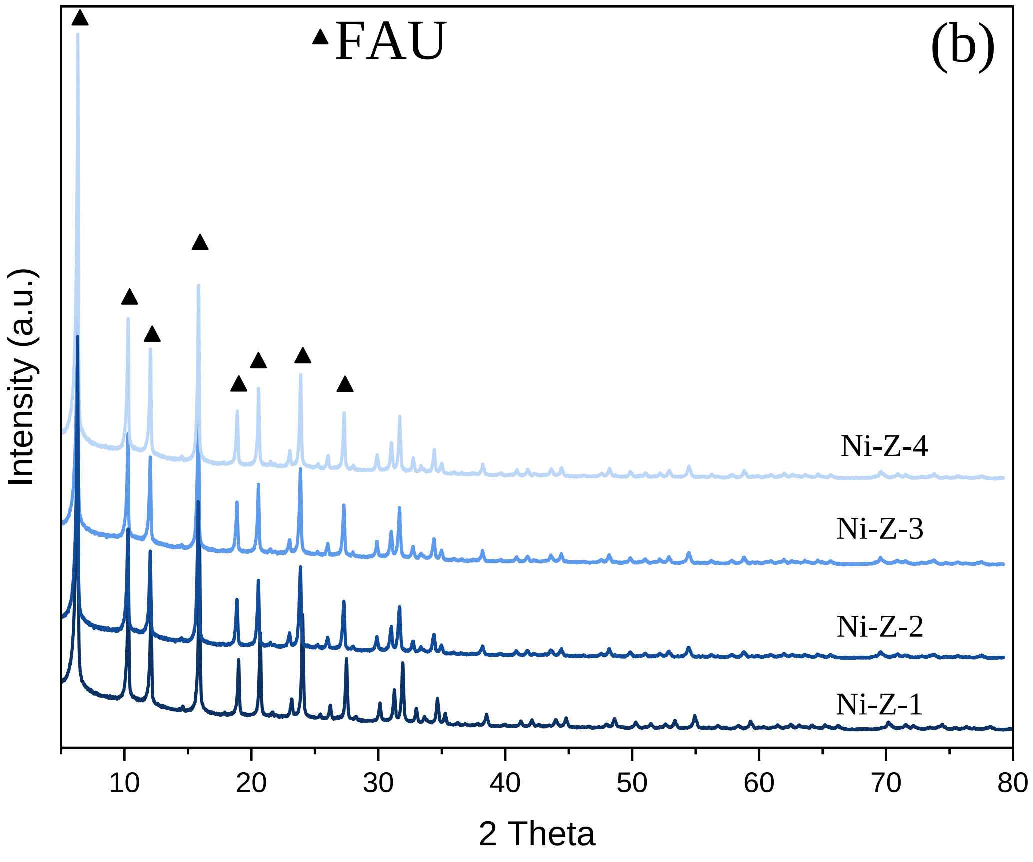




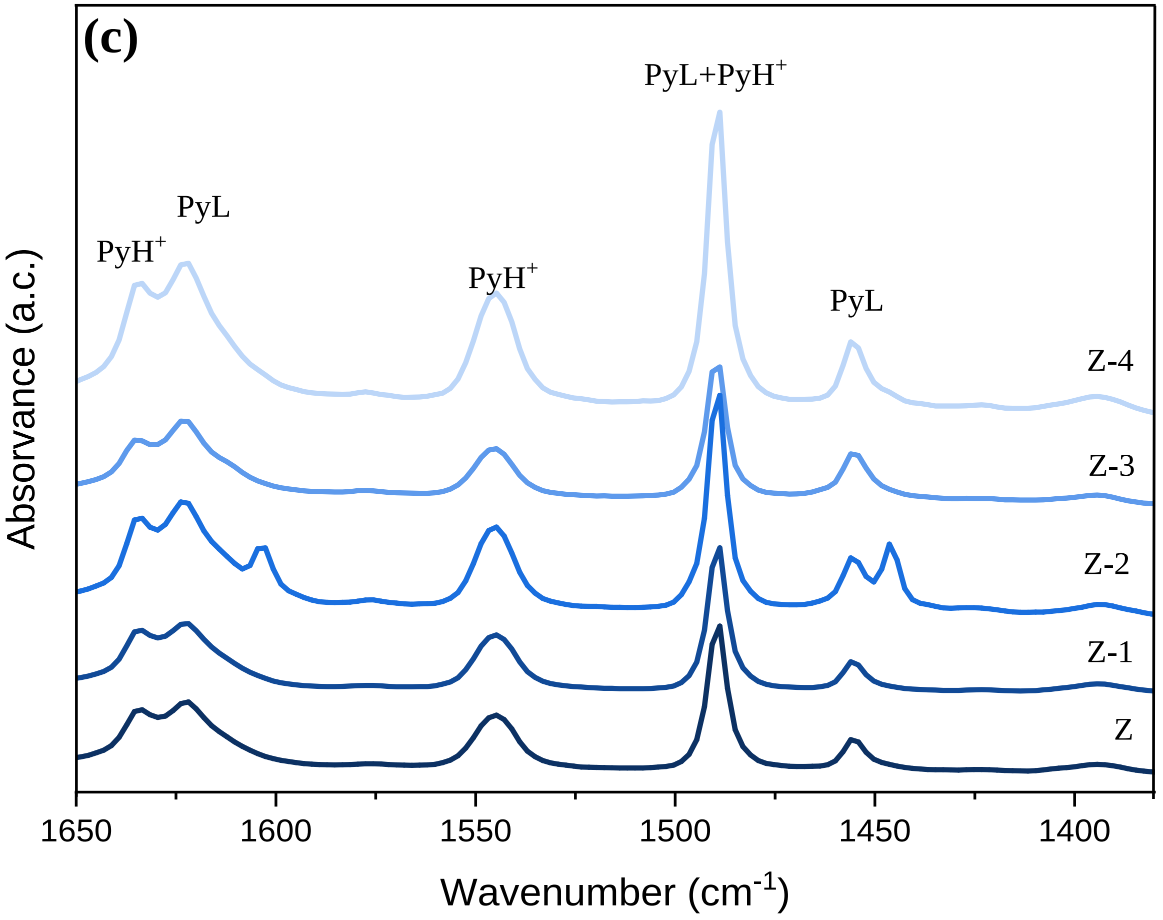


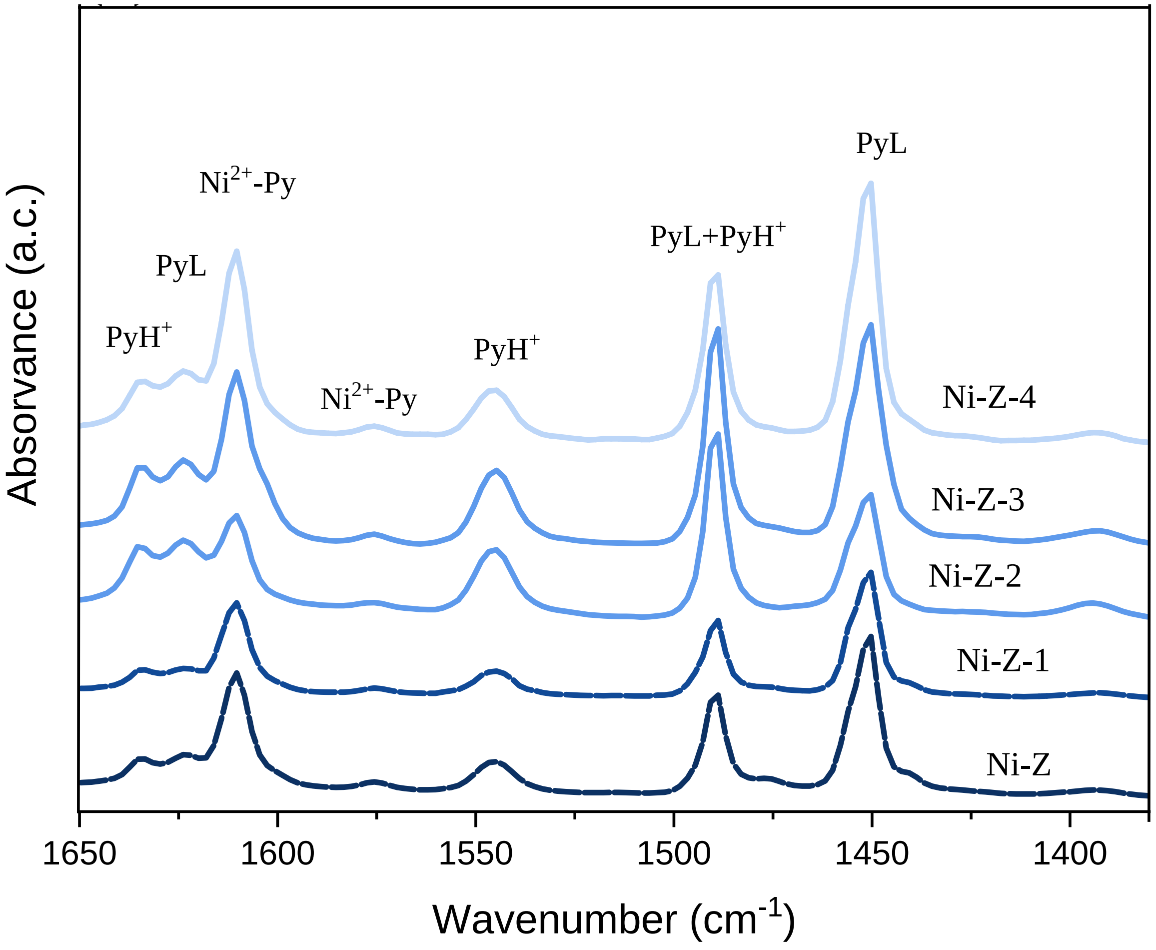
X-Ray Diffraction





Acidic Properties





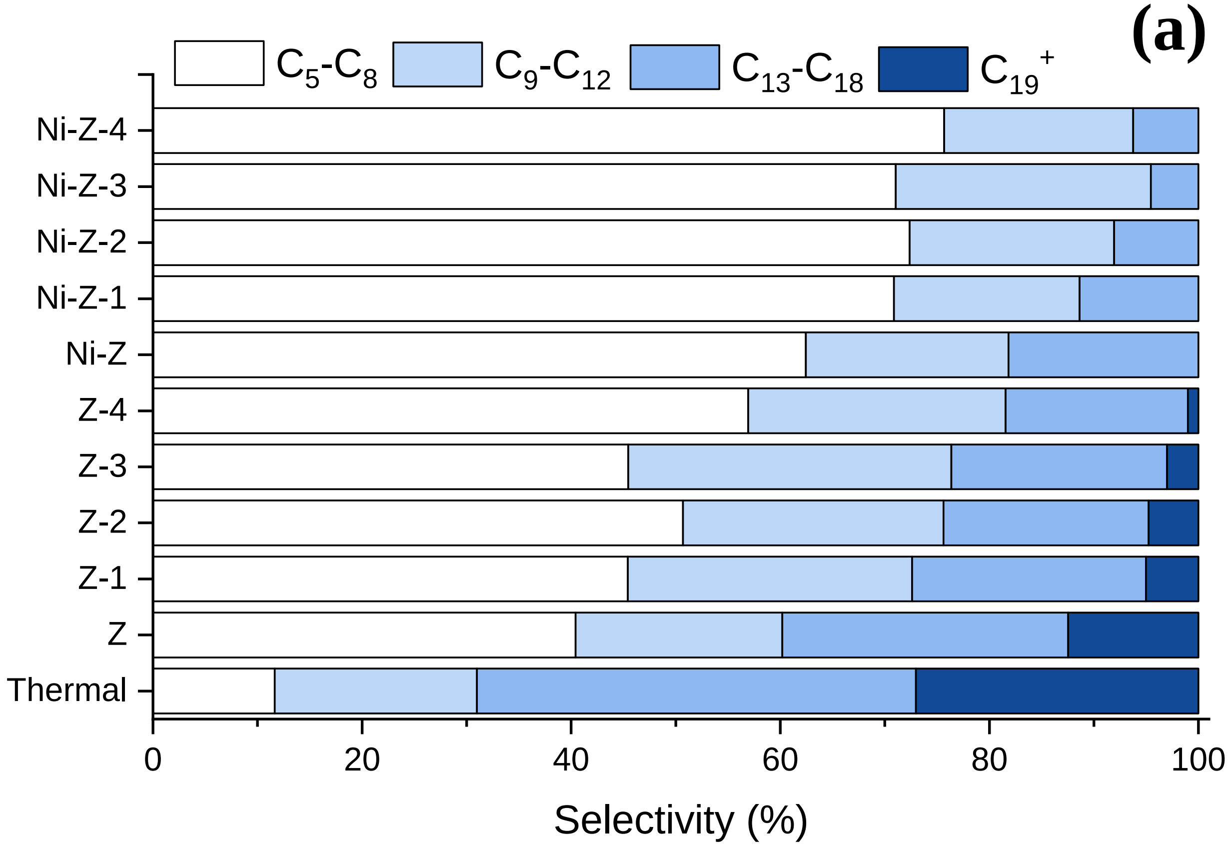
Physiochemical Properties

Catalyst Name	Relative intensity	Si/Al (ICP)	Si/Al_{IV} (XRD)	FAl	EFAl	PyH^+	PyL	$\frac{PyH^+{}_{350℃}}{PyH^+{}_{150℃}}$	$\frac{PyL_{350℃}}{PyL_{150℃}}$	V_{micro}	V_{meso}	S_{ext}
	%					$\mu molg^{-1}$		%	%	cm^3g^{-1}		m^2g^{-1}
Z	100	30	31	5.95	0.15	231	42	53	88	0.239	0.248	256
Z-1	93	29	29	6.34	0.07	237	36	47	89	0.272	0.283	297
Z-2	90	28	33	5.69	0.93	174	75	45	46	0.230	0.260	283
Z-3	87	37	39	4.76	0.29	116	47	28	73	0.239	0.282	301
Z-4	92	29	32	5.88	0.52	269	57	44	69	0.245	0.264	287
Ni-Z	96	-	-	-	-	123	263	37	34	0.227	0.224	241
Ni-Z-1	84	-	-	-	-	96	210	36	39	0.252	0.268	297
Ni-Z-2	82	-				137	178	35	29	0.237	0.260	281
Ni-Z-3	72	-	-	-	-	136	115	35	37	0.238	0.277	297
Ni-Z-4	83	-	-	-	-	114	250	34	36	0.222	0.255	286

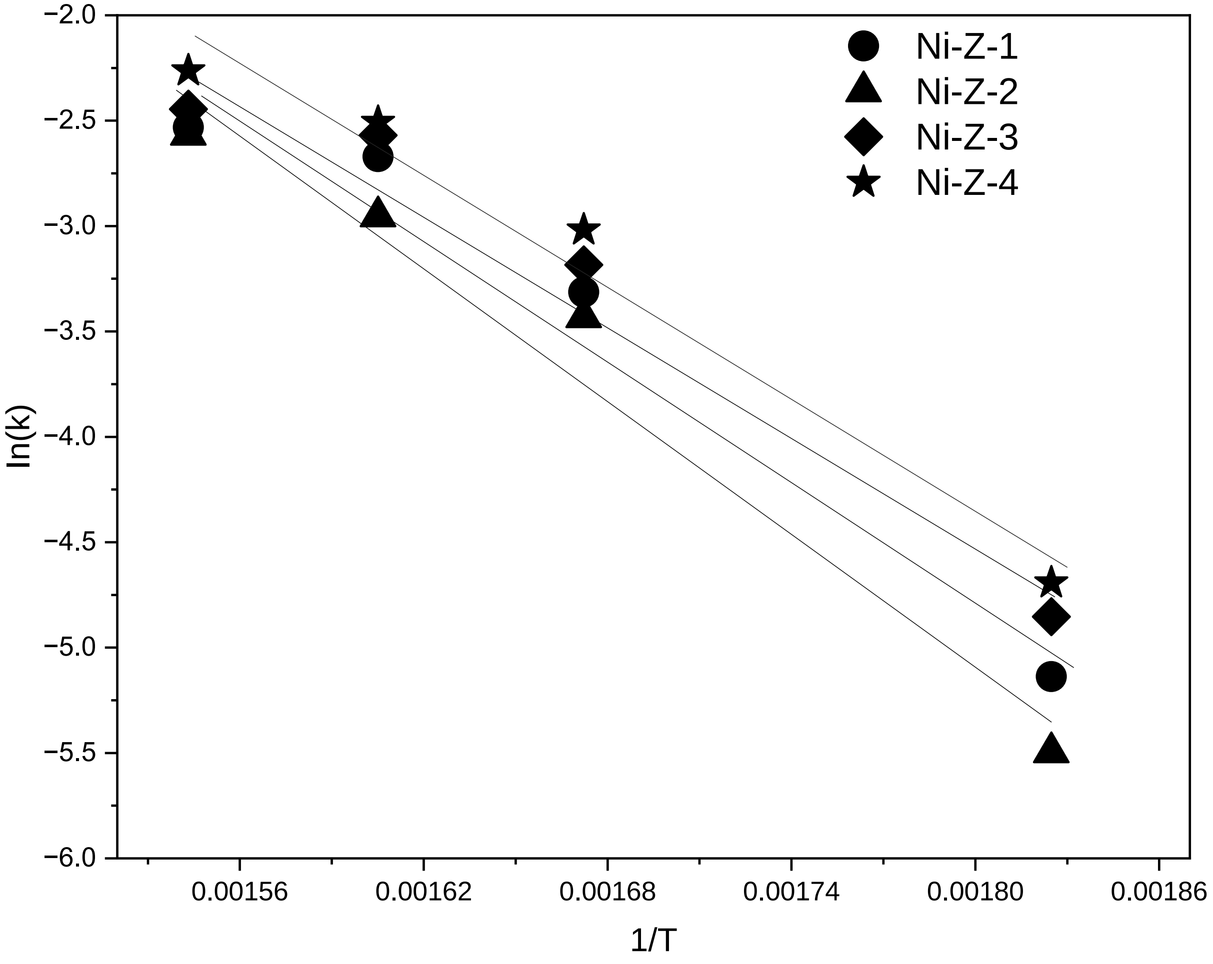
Hydrocracking of HDPE

Catalyst	Yield (%) (Selectivity (%))			Conv. (%)
	Gases	Lighter Oils	Heavier Oils	
Thermal	19.2 (42.9)	10 (22.3)	15.6 (34.8)	44.8
Z	22.8 (26.7)	55.3 (65.0)	7.1 (8.3)	86.5
Z-1	21.2 (23.7)	62.6 (69.9)	5.8 (6.4)	89.6
Z-2	21.0 (23.3)	63.6 70.6)	5.5 (6.1)	90.1
Z-3	25.7 (28.1)	61.2 (66.9)	4.7 (5.0)	91.6
Z-4	25.0 (26.9)	62.7 (67.8)	4.8 (5.2)	92.5
Ni-Z	28.5 (29.9)	60.9 (63.9)	6.0 (6.3)	95.3
Ni-Z-1	29.5 (29.8)	65.2 (65.7)	5.0 (5.1)	>99
Ni-Z-2	31.5 (31.8)	63.3 (63.9)	4.3 (4.4)	>99
Ni-Z-3	35.9 (36.0)	58.3 (58.6)	5.3 (5.4)	>99
Ni-Z-4	40.1 (40.1)	56.4 (56.5)	3.3 (3.3)	>99

Hydrocracking Experiment at 375 °C, 20 bar hydrogen pressure for 60 min residence time



Reaction Kinetics



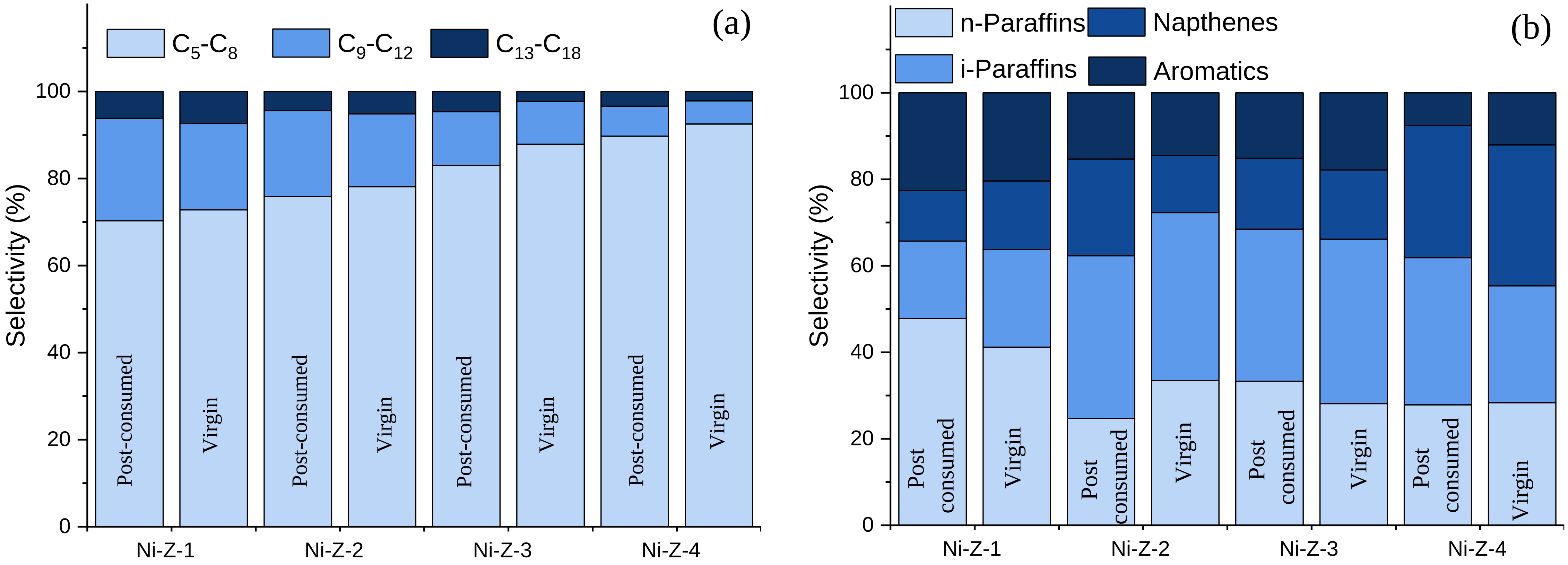
$$k = A.e^{\frac{E_a}{RT}}$$

Sample ID	R^2	E_a (kJ.mol^{-1})	A (min^{-1})
Ni-Z-1	0.97	88	1.2×10^6
Ni-Z-2	0.96	81	3.3×10^5
Ni-Z-3	0.96	75	1.1×10^5
Ni-Z-4	0.97	74	1.1×10^5

Post-Consumed Plastics

Catalyst	Material	Yield (%) (Selectivity (%))			Conv. (%)
		Gases	Lighter Oils	Heavier Oils	
Ni-Z-1	Post-consumed HDPE	26.63 (26.91)	64.86 (65.55)	7.46 (7.54)	98.95
	Virgin HDPE	26.14 (26.37)	66.17 (66.77)	6.79 (6.86)	>99
Ni-Z-2	Post-consumed HDPE	28.66 (28.86)	63.73 (64.42)	6.91 (6.95)	>99
	Virgin HDPE	31.16 (31.22)	62.52 (62.65)	6.11 (6.12)	>99
Ni-Z-3	Post-consumed HDPE	30.28 (30.46)	62.89 (63.27)	6.23 (6.27)	>99
	Virgin HDPE	33.34 (33.47)	60.33 (60.57)	5.93 (5.95)	>99
Ni-Z-4	Post-consumed HDPE	33.44 (33.64)	60.17 (60.53)	5.99 (6.03)	99
	Virgin HDPE	36.88 (36.91)	57.60 (57.66)	5.42 (5.43)	>99

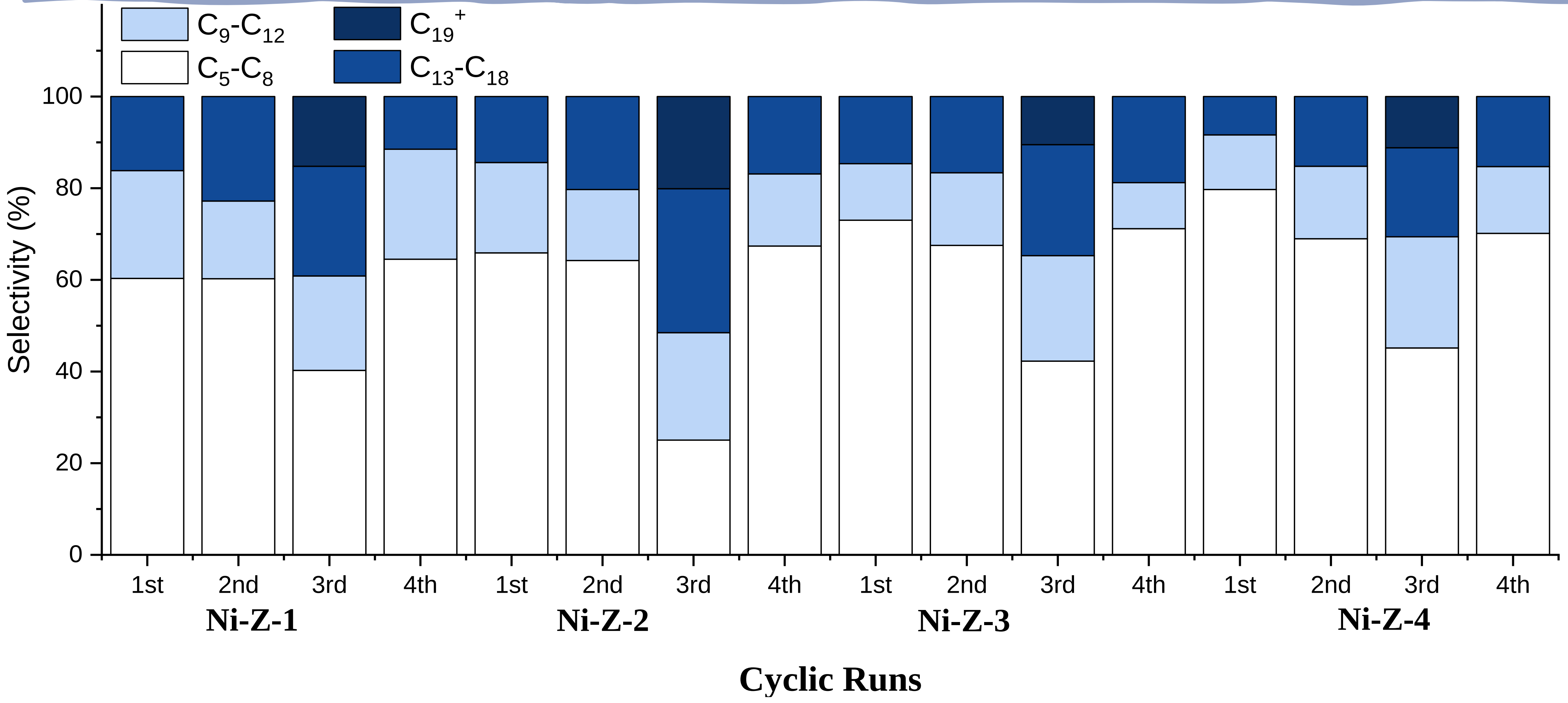
Post-Consumed Plastics



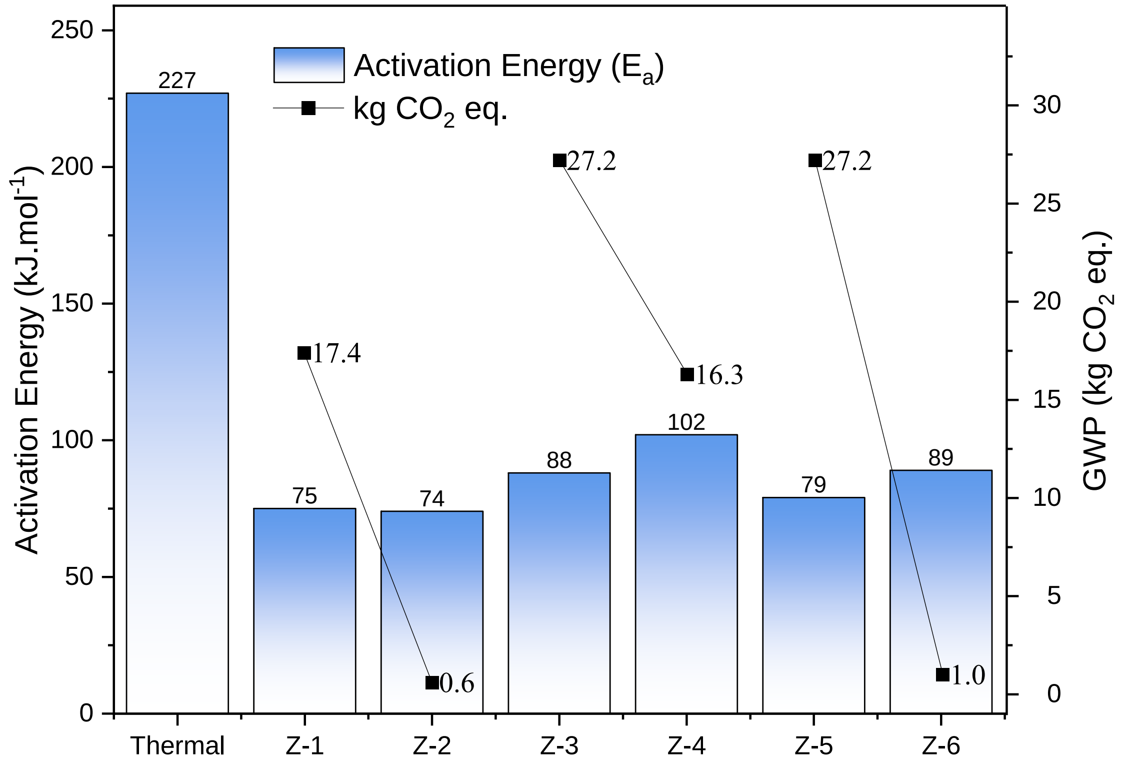
Reusability

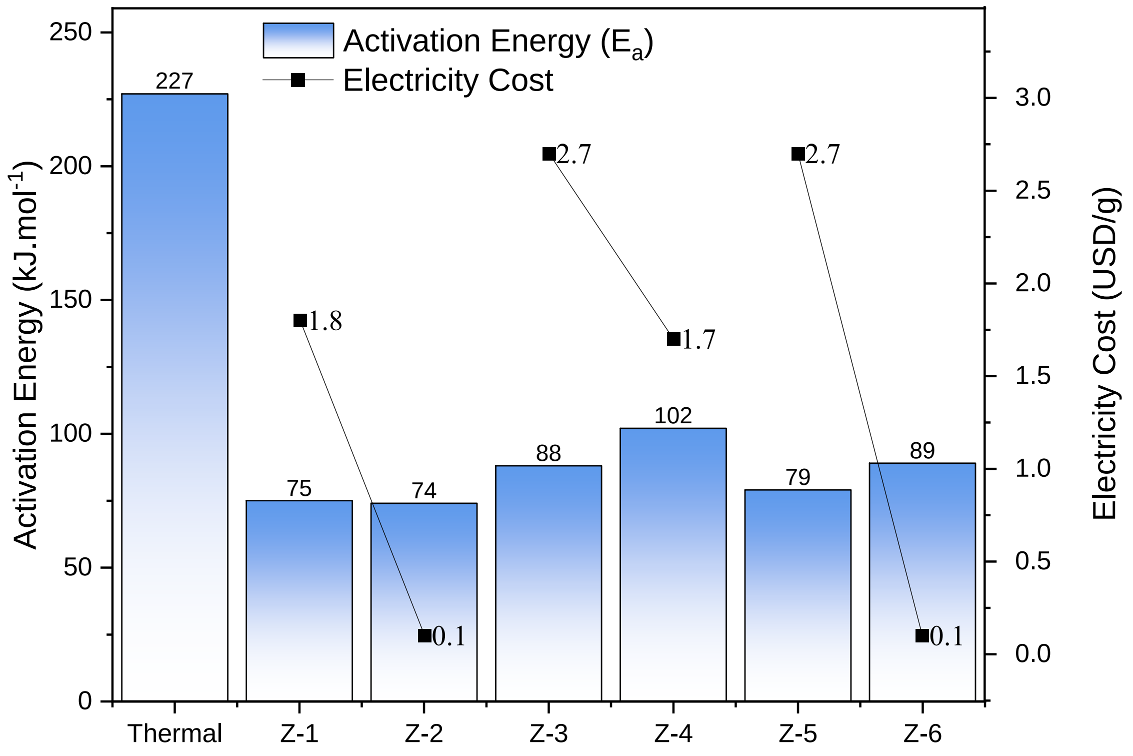
Catalyst	Material	Yield (%) (Selectivity (%))			Conv. (%)
		Gases	Lighter Oils	Heavier Oils	
Ni-Z-1	Fresh Run	26.6 (26.9)	64.9 (65.6)	7.4 (7.5)	98.95
	Spent I	24.6 (26.5)	58.2 (62.8)	10.0 (10.8)	92.8
	Spent II	23.9 (27.2)	48.6 (55.2)	15.4 (17.5)	87.89
	Regenerated Run	23.4 (24.6)	60.8 (64.1)	10.7 (11.2)	94.79
Ni-Z-2	Fresh Run	28.7 (28.9)	63.7 (64.4)	6.9 (7.0)	>99
	Spent I	24.4 (25.6)	62.7 (65.7)	8.3 (8.7)	95.38
	Spent II	21.4 (25.2)	47.5 (55.9)	16.0 (18.8)	84.82
	Regenerated Run	21.2 (22.1)	61.6 (64.4)	12.8 (13.4)	95.57
Ni-Z-3	Fresh Run	30.3 (30.5)	62.9 (63.3)	6.2 (6.3)	>99
	Spent I	26.1 (27.2)	62.7 (65.3)	7.2 (7.5)	95.88
	Spent II	23.6 (26.2)	55.8 (61.8)	10.8 (12.0)	90.17
	Regenerated Run	30.2 (31.2)	58.9 (60.9)	7.6 (7.9)	96.67
Ni-Z-4	Fresh Run	33.4 (33.6)	60.2 (60.5)	6.0 (6.0)	>99
	Spent I	23.3 (24.0)	64.0 (65.8)	9.9 (10.2)	97.20
	Spent II	21.9 (23.7)	58.5 (63.2)	12.2 (13.2)	92.65
	Regenerated Run	31.9 (32.6)	59.1 (60.4)	6.8 (7.0)	97.82

Reusability



Sustainable Catalysis: Other Zeolite Based Supports





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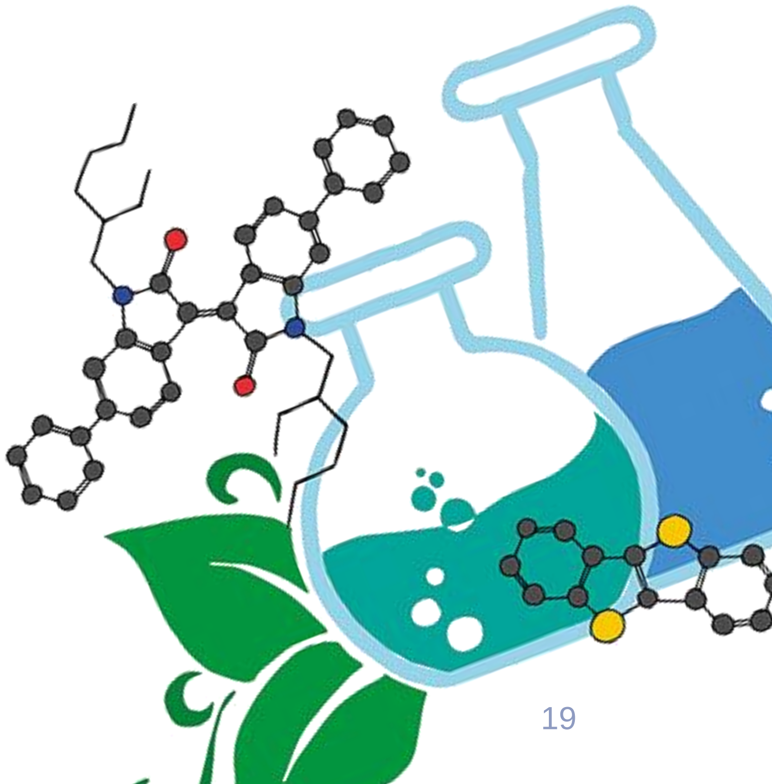
Conclusion

- Sustainable Catalysis
- Low energy requirements
- High quality gasoline range fuels
- High reusability of spent catalysts
- Provide new direction to industries



References

- Azam, M. U., Vete, A., & Afzal, W. (2022). Process simulation and life cycle assessment of waste plastics: a comparison of pyrolysis and hydrocracking. *Molecules*, *27*(22), 8084.
- Azam, M. U., Fernandes, A., Graça, I., & Afzal, W. (2023). Hydrocracking of surgical face masks over Y Zeolites: Catalyst development, process design and life cycle assessment. *Fuel*, *349*, 128704.

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