Genesys-Cat: Automatic Microkinetic Model Generation for Heterogeneous Catalysis with Improved Bayesian Optimization

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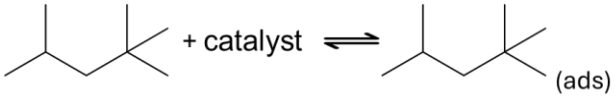
Supporting Information

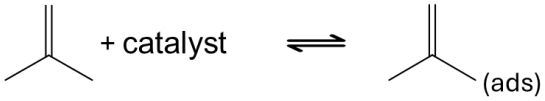
S1. Considered Reaction Families

A total of 23 reaction families are considered for the modelling of the catalytic cracking of iso-octane. These are presented below with an example reaction for illustration.

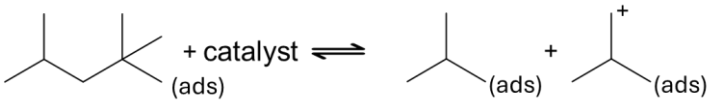
1/ Physisorption of alkanes



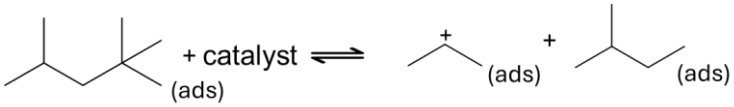
2/ Physisorption of alkenes



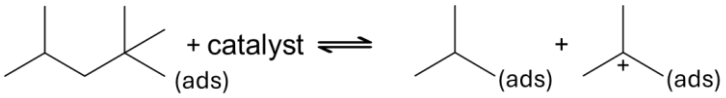
3/ Protolytic scission (primary ion product)



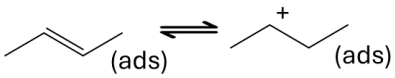
4/ Protolytic scission (secondary ion product)



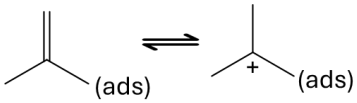
5/ Protolytic scission (tertiary ion product)



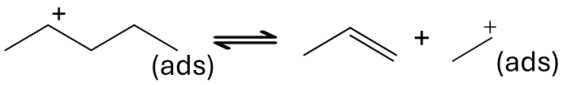
6/ Protonation olefins (secondary ion product)



7/ Protonation olefins (tertiary ion product)



8/ β-scission (primary ion product)



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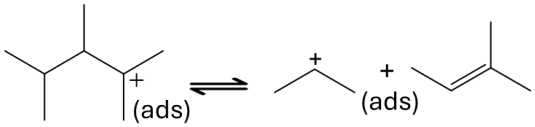
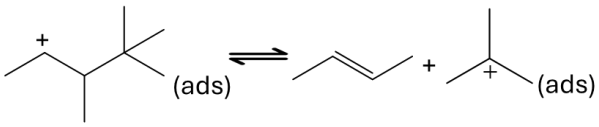
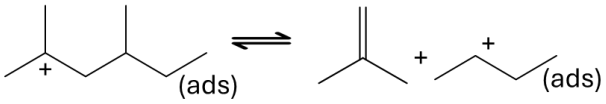


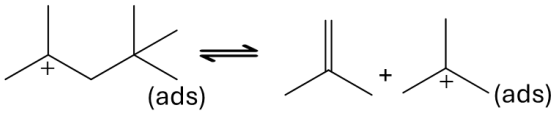
10/ β-scission (secondary ion reactant, tertiary ion product)



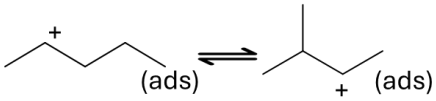
11/ β-scission (tertiary ion reactant, secondary ion product)



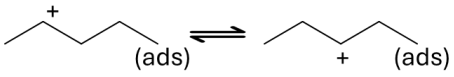
12/ β-scission (tertiary ion reactant, tertiary ion product)



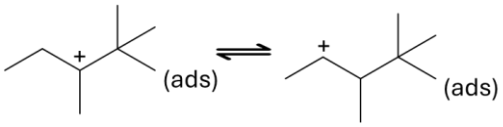
13/ PCP-Branching (secondary ion reactant, secondary ion product)



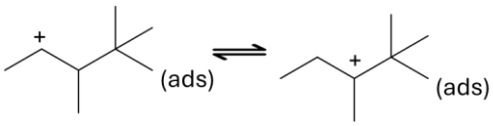
14/ 1,2-Intramolecular hydrogen-shift (secondary ion reactant, secondary ion product)



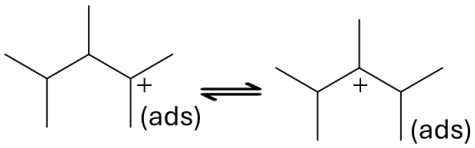
15/ 1,2-Intramolecular hydrogen-shift (tertiary ion reactant, secondary ion product)



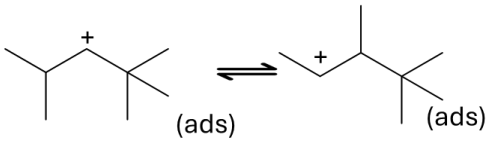
16/ 1,2-Intramolecular hydrogen-shift (secondary ion reactant, tertiary ion product)



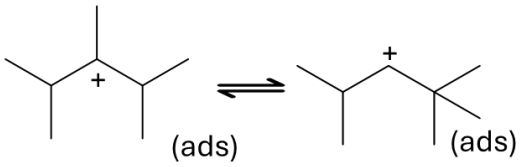
17/ 1,2-Intramolecular hydrogen-shift (tertiary ion reactant, tertiary ion product)



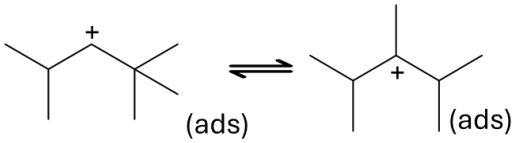
18/ 1,2-Intramolecular methyl-shift (secondary ion reactant, secondary ion product)



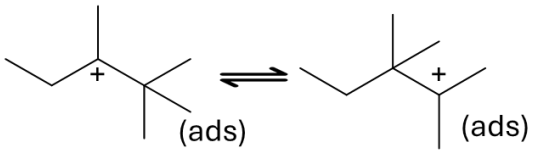
19/ 1,2-Intramolecular methyl-shift (tertiary ion reactant, secondary ion product)



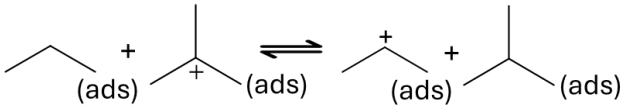
20/ 1,2-Intramolecular methyl-shift (secondary ion reactant, tertiary ion product)



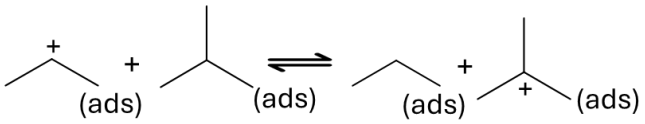
21/ 1,2-Intramolecular methyl-shift (tertiary ion reactant, tertiary ion product)



22/ Intermolecular hydrogen abstraction (secondary product)



23/ Intermolecular hydrogen abstraction (tertiary product)



S2. Catalyst Properties for Iso-octane Cracking

Zeolite properties including Si/Al-ratios, concentration of acid sites (C_t) measured by NH_3-TPD, internal catalyst area (S_{BET}) and micropore volume (V_{micro}). More information on the zeolite characterization can be found in the work of Van Borm et al. [1].

Table S1. Zeolite properties as reported in [1].

Zeolite (Topology)	Si/Al_{bulk}	Si/Al_{frame}	C_t (mol kg_{cat}^{-1})	S_{BET} (m^2 g_{cat}^{-1})	V_{micro} (cm^3 g_{cat}^{-1})
LZY20 (FAU)	2.6	30.0	0.99	481	0.19
CBV720 (FAU)	15	16.0	0.60	673	0.27
CBV760 (FAU)	30	100	0.23	526	0.25

S3. Parameter Ranges of the Activation Entropy Estimation

Table S2. Employed parameter ranges of the activation entropy for Levenberg-Marquardt and Bayesian optimization.

	$\Delta^{\ddagger}S$ [J mol^{-1} K^{-1}]		$\Delta^{\ddagger}S$ [J mol^{-1} K^{-1}]
Physisorption (alkanes)	-190 to -100	Physisorption (alkenes)	-190 to -100
Protolytic scission (p)	-180 to -110	β-scission (p)	-120 to 0
Protolytic scission (s)	-180 to -110	β-scission (s,s)	-120 to 0
Protolytic scission (t)	-180 to -110	β-scission (s,t)	-120 to 0
Hydride-transfer (s)	-100 to 50	β-scission (t,s)	-120 to 0
Hydride-transfer (t)	-100 to 50	β-scission (t,t)	-120 to 0

S4. Pre-exponential Factors of the CBV720 and CBV760 Kinetic Model

Table S3. Pre-exponential factors optimized by improved Bayesian optimization for CBV720

	A [s^{-1}]		A [s^{-1}]
Physisorption (alkanes)	$1.81\ 10^{1}$ (*)	Physisorption (alkenes)	$3.15\ 10^{2}$ (*)
Protolytic scission (p)	$5.23\ 10^{6}$	β-scission (p)	$8.66\ 10^{7}$
Protolytic scission (s)	$7.86\ 10^{5}$	β-scission (s,s)	$3.78\ 10^{7}$
Protolytic scission (t)	$8.86\ 10^{5}$	β-scission (s,t)	$1.63\ 10^{11}$
Hydride-transfer (s)	$2.43\ 10^{4}$	β-scission (t,s)	$1.12\ 10^{9}$
Hydride-transfer (t)	$2.07\ 10^{6}$	β-scission (t,t)	$1.59\ 10^{9}$

(*) [l mol^{-1} s^{-1}]

Table S4. Pre-exponential factors optimized by improved Bayesian optimization for CBV760

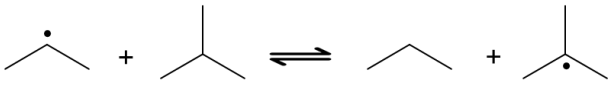
	A [s^{-1}]		A [s^{-1}]
Physisorption (alkanes)	$1.81\ 10^{1}$ (*)	Physisorption (alkenes)	$3.15\ 10^{2}$ (*)
Protolytic scission (p)	$5.23\ 10^{6}$	β-scission (p)	$1.58\ 10^{8}$
Protolytic scission (s)	$7.86\ 10^{5}$	β-scission (s,s)	$3.78\ 10^{7}$
Protolytic scission (t)	$8.86\ 10^{5}$	β-scission (s,t)	$1.63\ 10^{11}$
Hydride-transfer (s)	$1.19\ 10^{4}$	β-scission (t,s)	$1.12\ 10^{9}$
Hydride-transfer (t)	$1.01\ 10^{6}$	β-scission (t,t)	$1.59\ 10^{9}$

(*) [l mol^{-1} s^{-1}]

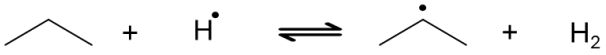
S5. Reaction Families for Coupled Gas and Surface Phase Mechanism of Thermal and Catalytic 1-Butene Cracking

A total of 13 reaction families are considered for the modelling of the thermal and catalytic cracking of 1-butene. These are presented below with an example reaction for illustration.

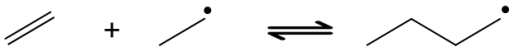
1/ Hydride abstractions to a carbon centered group by a carbon centered radical (gas-phase)



2/ Hydride abstractions to a carbon centered group by a hydrogen radical (gas-phase)

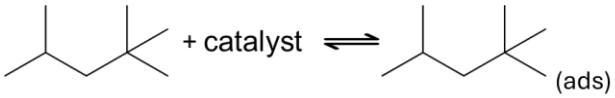


3/ Carbon-Centered Radical Addition (gas-phase)

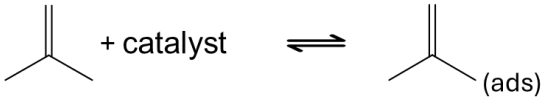


4/ Hydrogen Radical Addition (gas-phase)

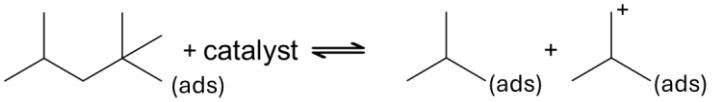
5/ Physisorption of alkanes (surface-phase)



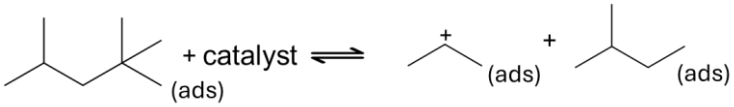
6/ Physisorption of alkenes (surface-phase)



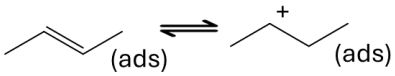
7/ Protolytic scission (primary ion product) (surface-phase)



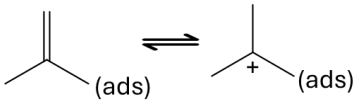
8/ Protolytic scission (secondary ion product) (surface-phase)



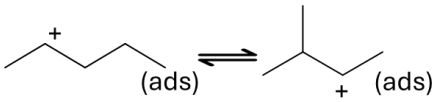
9/ Protonation olefins (secondary ion product) (surface-phase)



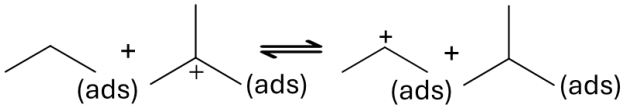
10/ Protonation olefins (tertiary ion product) (surface-phase)



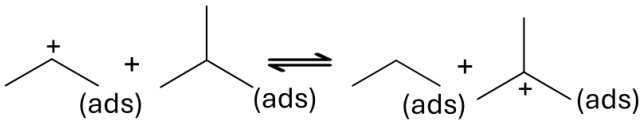
11/ PCP-Branching (surface-phase)



12/ Intermolecular hydrogen abstraction (secondary product) (surface-phase)



13/ Intermolecular hydrogen abstraction (tertiary product) (surface-phase)



S6. Residual Conversion with Varying Temperature

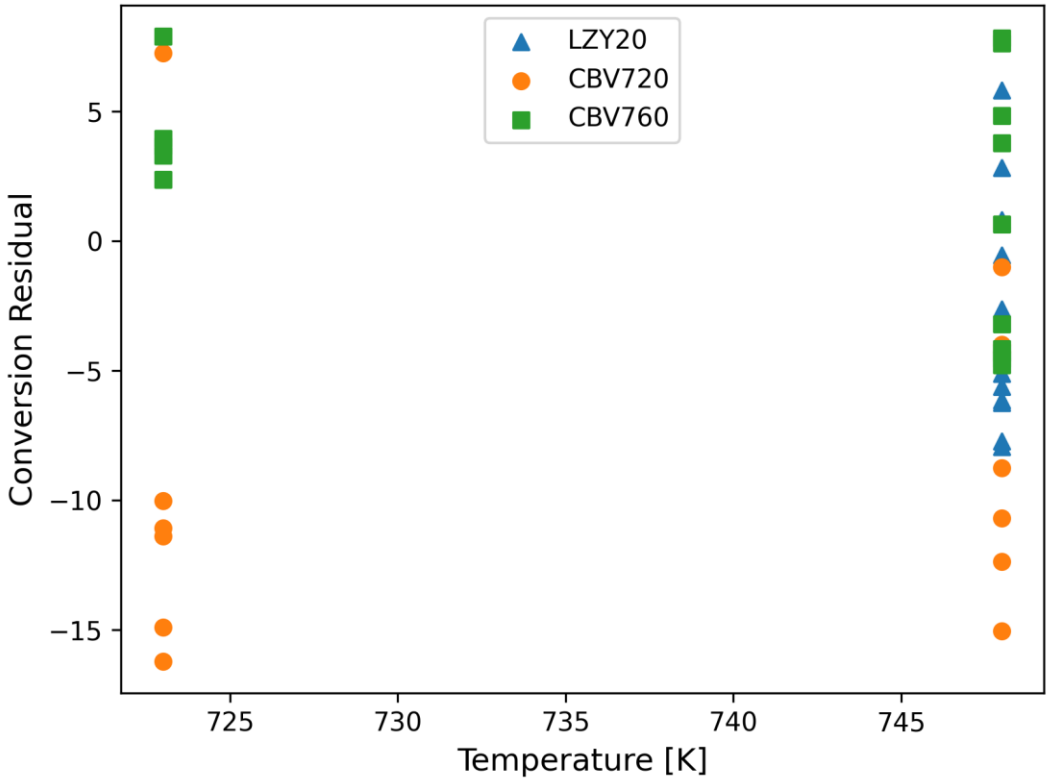


Figure S1. Residual conversion defined as difference between predicted and experimental conversion with varying temperature.

S7. Experimental and Predict Molar Selectivities of Other Products

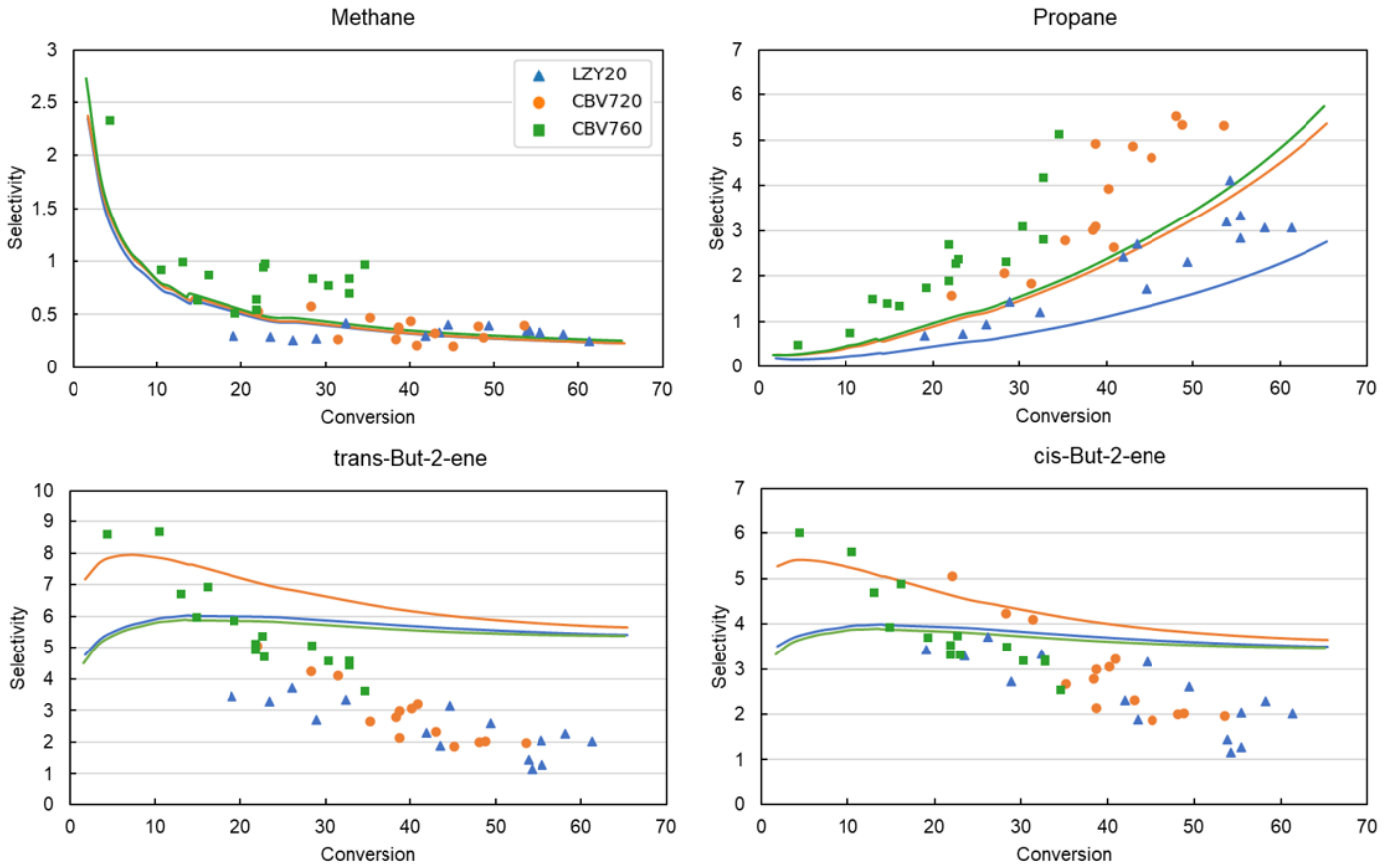


Figure S2. Experimental (markers) vs. predicted (lines) selectivities of methane, propane, trans-but-2-ene, and cis-but-2-ene for iso-octane catalytic cracking in LZY20, CBV720 and CBV760 as function of conversion.

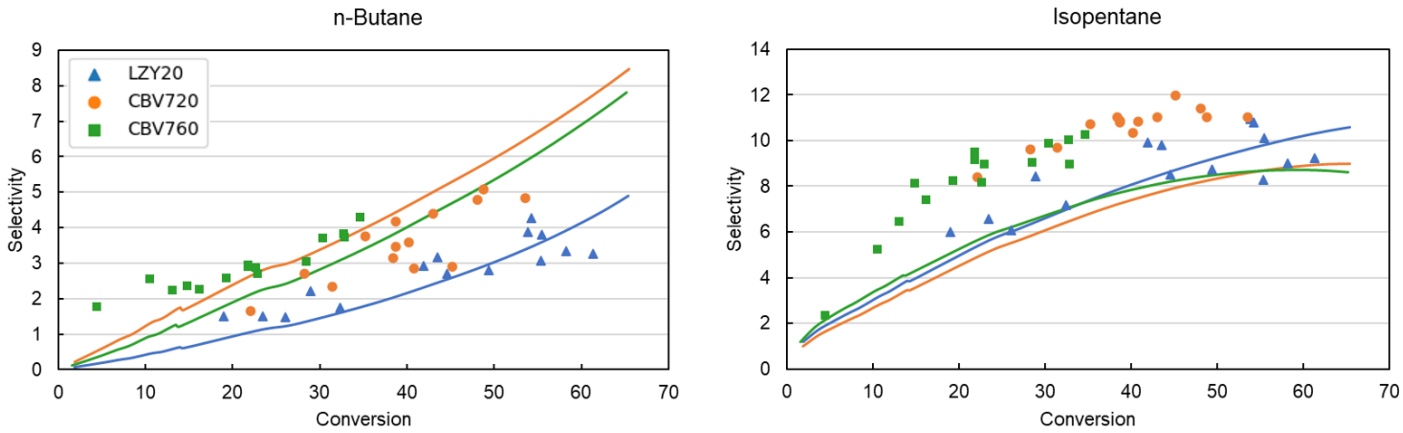


Figure S3. Experimental (markers) vs. predicted (lines) selectivities of n-butane and isopentane for iso-octane catalytic cracking in LZY20, CBV720 and CBV760 as function of conversion.

References

[1] Van Borm R, Aerts A, Reyniers M-F, Martens JA, Marin GB. Catalytic cracking of 2, 2, 4-trimethylpentane on FAU, MFI, and bimodal porous materials: influence of acid properties and pore topology. Industrial & engineering chemistry research 2010;49(15):6815-23.