

Supporting Information

Multi-scale Modeling as a Tool for the Prediction of Catalytic Performances: the Case of n-Heptane Hydroconversion in a Large Pore Zeolite

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S1. Limitation of the reaction kinetics by the acidic phase: experimental evidence.

The impact of the total pressure on the bifunctional catalyst activity can be used as an experimental tool to assess if the reaction kinetics are limited by the acidic or metallic phase.¹ Indeed, if the hydro/dehydrogenation reactions are at equilibrium, increasing the total pressure should decrease the catalyst activity as a thermodynamic effect is at stake. At higher pressure the concentration of alkene and so the concentration of carbenium ions is lowered according to Le Chatelier principle. Experiments were performed at 230°C and three different total pressures (Figure S1). The increase of total pressure clearly decreased the catalyst activity. Based on the initial slope of the curves, the catalyst activity was estimated to $2 \cdot 10^{-2} \text{ mol C}_7 \text{ g cat}^{-1} \text{ h}^{-1}$ at 5 barg total pressure, $1,5 \cdot 10^{-2} \text{ mol C}_7 \text{ g cat}^{-1} \text{ h}^{-1}$ at 10 barg total pressure and $1 \cdot 10^{-2} \text{ mol C}_7 \text{ g cat}^{-1} \text{ h}^{-1}$ at 15 barg total pressure.

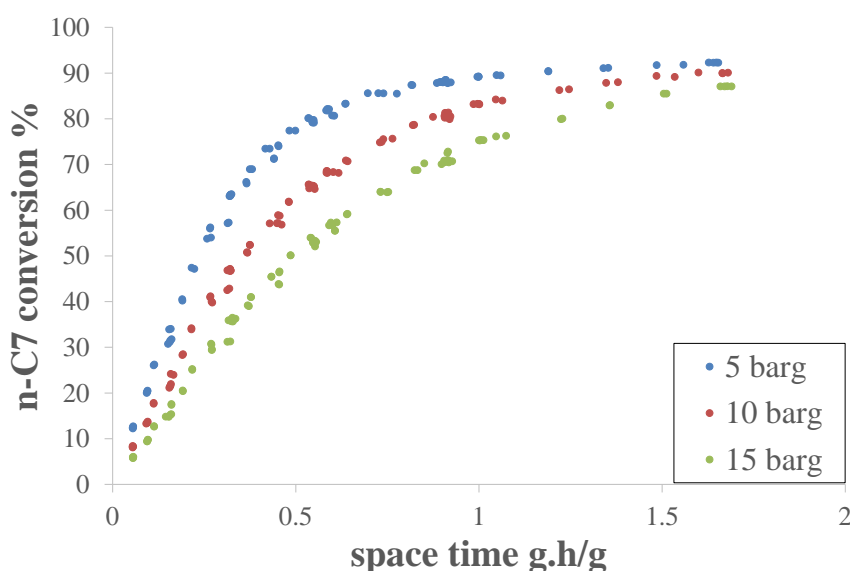


Figure S1. Evolution of the conversion with space time for the sixteen reactors of the HTE unit at 230°C and various total pressures (10 barg; $\text{H}_2/\text{n-C}_7$ 10 mol /mol).

S2. Validation of HTE kinetic experiments

The absence of significant hydrodynamic effect was checked experimentally, by loading different amount of catalyst in the various reactors. During the catalytic test, the n-heptane and hydrogen flow rates were also varied. It was then possible to plot the evolution of the conversion with space time at various temperatures for the sixteen reactors of the HTE unit (Figure S2). The n-heptane conversion was only marginally impacted by the amount of catalyst (and so by the gas phase space velocity) for a given space time at a given temperature.

Similarly, the evolution of heptane isomers yield with n-heptane conversion follow a unique curve for a given temperature (Figure S3). The catalyst selectivity was not impacted by the amount of loaded catalyst.

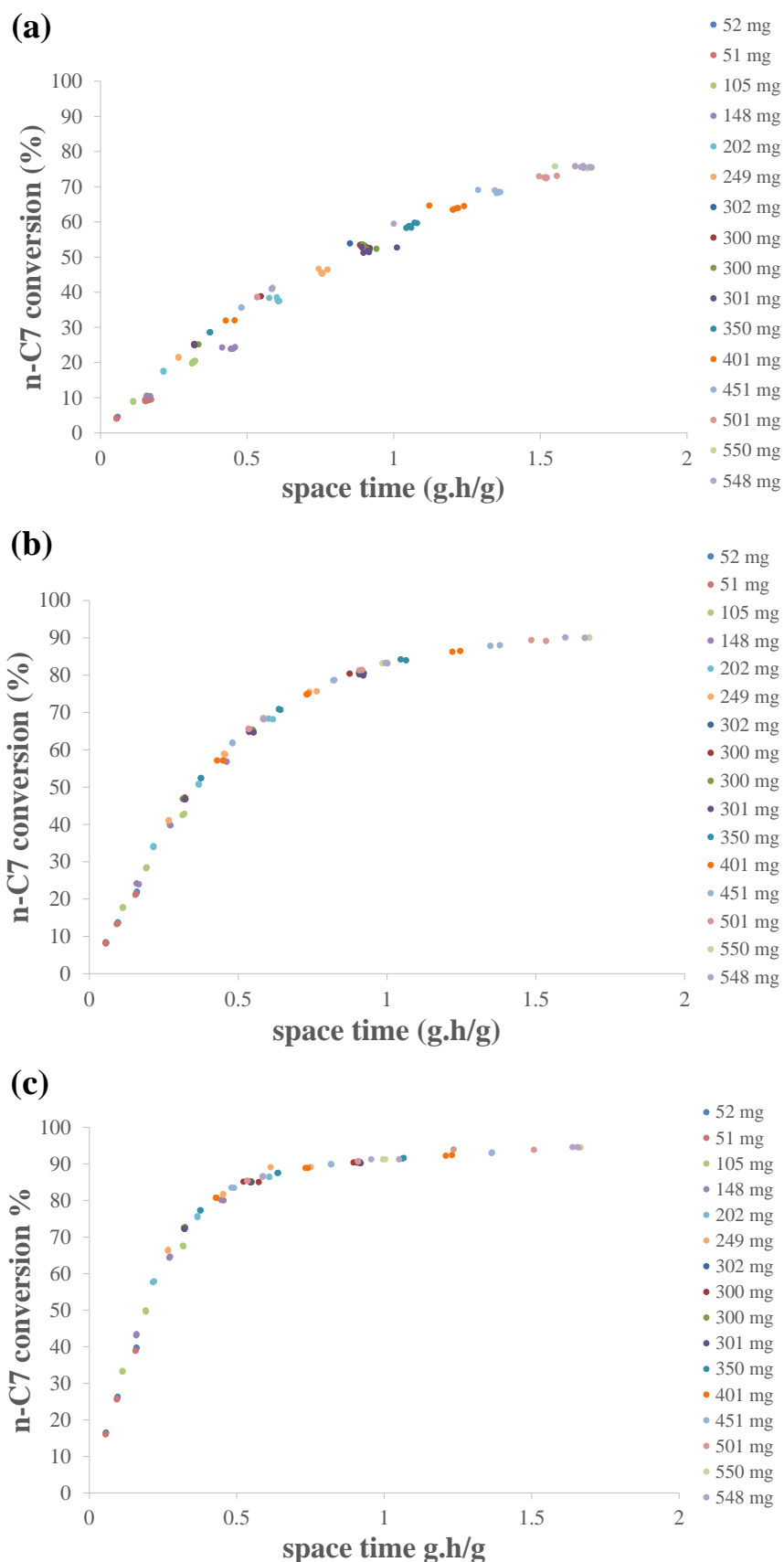


Figure S2. Evolution of the conversion with space time for the sixteen reactors of the HTE unit at (a) 220°C; (b) 230°C and (c) 240°C (10 barg; $H_2/n-C_7$ 10 mol /mol). The amount of catalyst loaded in each reactor is reported in the legend.

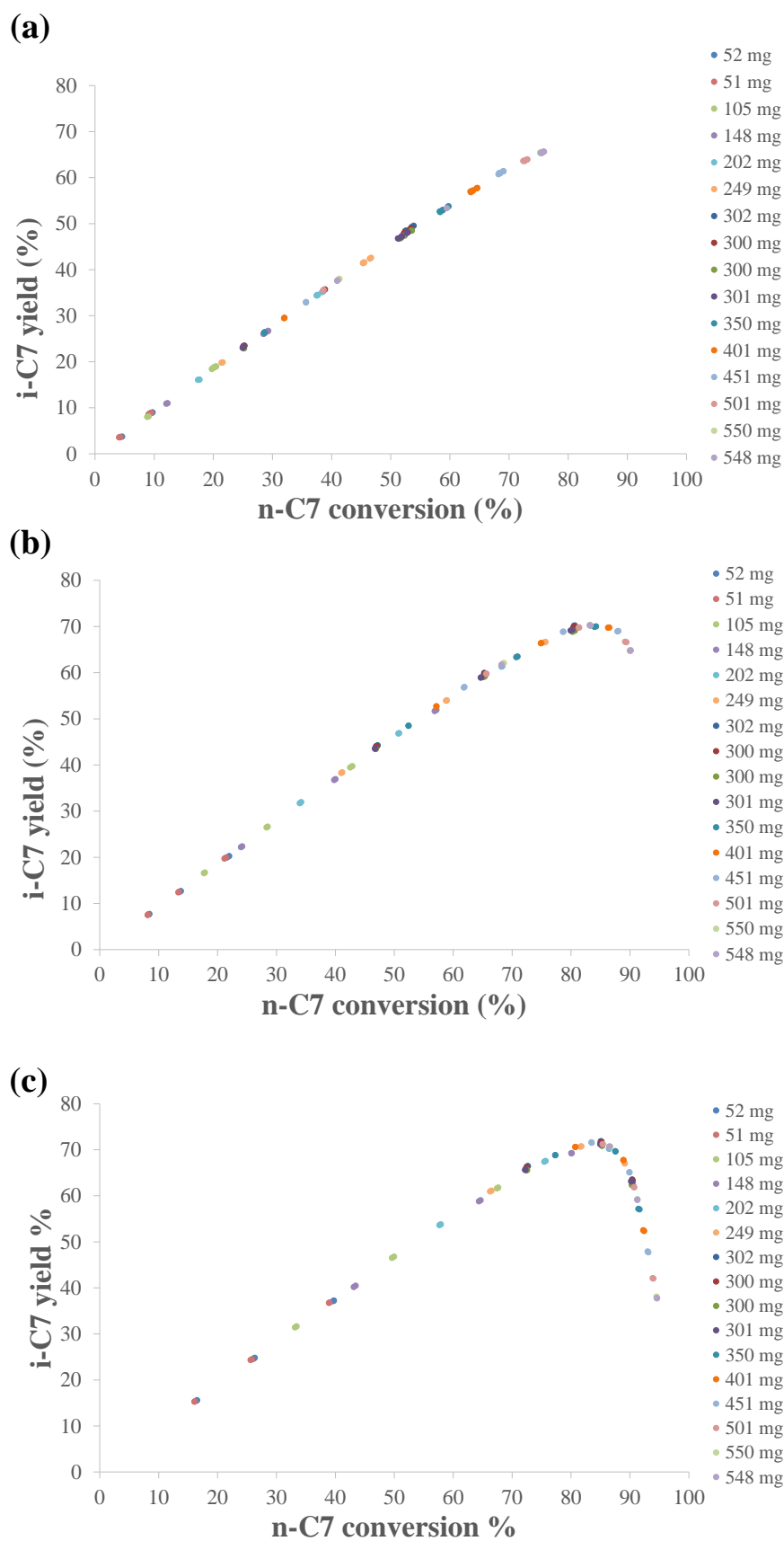


Figure S3. Evolution of heptane isomers yield with conversion for the sixteen reactors of the HTE unit at (a) 220°C; (b) 230°C and (c) 240°C (10 barg; $H_2/n-C_7$ 10 mol/mol). The amount of catalyst loaded in each reactor is reported in the legend.

S3. Complete reaction network for n-heptane hydrocracking

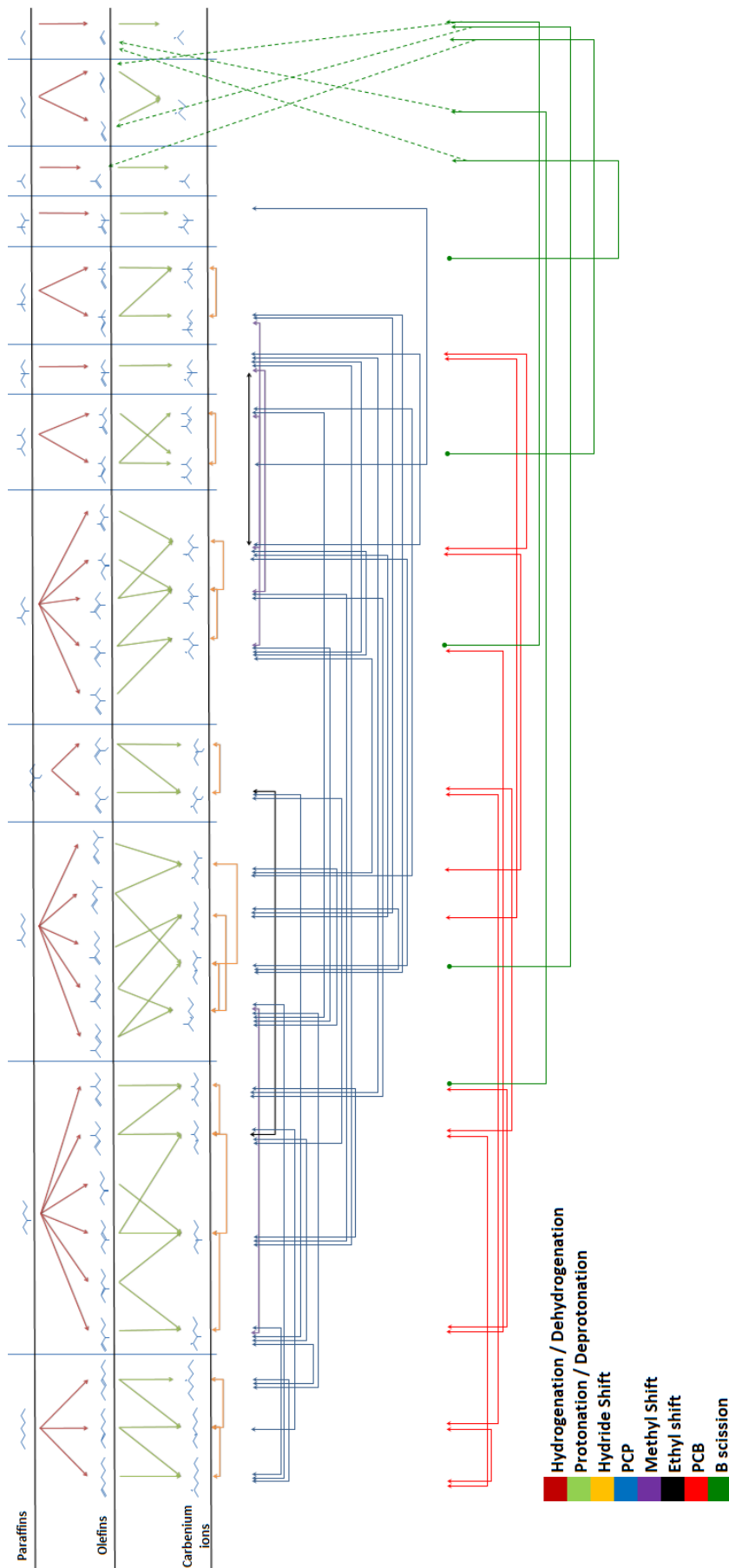


Figure S4. Hydrocracking of n-heptane: elementary steps of the reaction network.

S4. Complementary experimental catalytic features

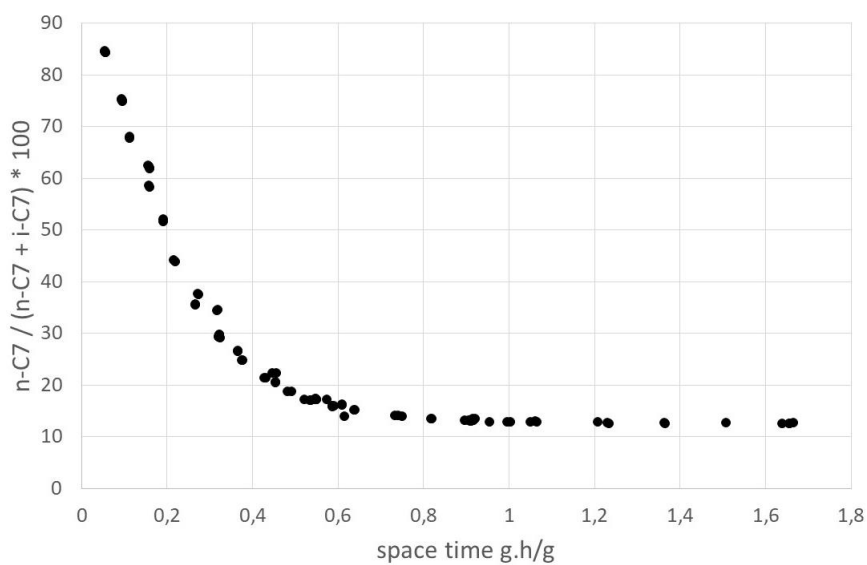


Figure S5. Evolution of the n-heptane percentage in the n and iso-heptanes with space time. 240°C, $H_2/n-C_7$ 10 mol/mol, 10 barg.

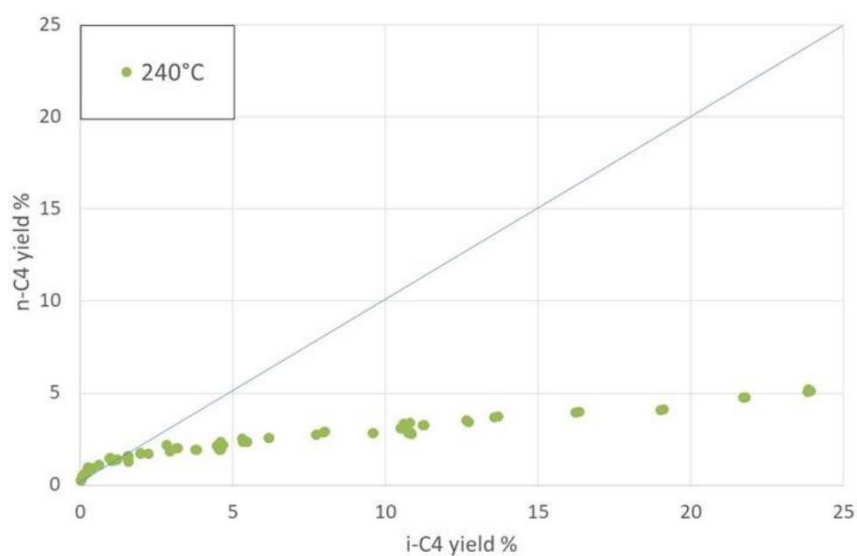


Figure S6. n-butane yield as a function of isobutane yield at 240°C, $H_2/n-C_7$ 10 mol/mol, 10 barg.

S5. Kinetic data obtained from DFT calculations

Table S1. Adsorption parameters (equilibrium constant, adsorption enthalpy, entropy and free energy) of 4-methylhex-1-ene computed by static DFT at 227°C.

K	$\Delta_r H$ (kJ/mol)	$\Delta_r S$ (J/mol/K)	$\Delta_r G$ (kJ/mol)
942.7	-111.1	-165	-28

Table S2. Protonation free energy of π -complexes obtained by AIMD at 227°C. Data extracted from previous works.²⁻³

Protonation	$\Delta_r G$ (kJ/mol)
π -complex \rightarrow secondary carbenium*	45 \pm 10
π -complex \rightarrow tertiary carbenium**	-15 \pm 10

* Estimation based on calculations done for the protonation of 4-methyl-1-hexene² and of 4,4-dimethyl-pent-2-ene⁴

** Estimation based on calculations done for the stability of various tertiary cations as reported in^{2,4}

Table S3. Activation parameters (enthalpy, entropy and free energy, rate constants) at 227°C determined by static DFT for type B isomerization reactions, in the forward (+ subscript) and backward (- subscript) directions, according to the terminology given in Figure 1.

TS corresponding to the reaction	$\Delta_r H_{+}^{\ddagger}$ (kJ/mol)	$\Delta_r H_{-}^{\ddagger}$ (kJ/mol)	$\Delta_r S_{+}^{\ddagger}$ (J/mol/K)	$\Delta_r S_{-}^{\ddagger}$ (J/mol/K)	$\Delta_r G_{+}^{\ddagger}$ (kJ/mol)	$\Delta_r G_{-}^{\ddagger}$ (kJ/mol)	k_{+} (s ⁻¹)	k_{-} (s ⁻¹)
TS1a	21.9	32.8	-22.5	-16.6	33.2	41.1	3.6e+9	5.3e+8
TS1b	28.7	31.8	-18.6	-26.8	38.0	45.2	1.1e+9	2.0e+8
TS2	22.3	33.2	-24.5	-26.0	34.6	46.2	2.6e+9	1.5e+8
TS3a	62.9	69.4	-45.6	-28.7	85.7	83.7	1.2e+4	1.9e+4
TS3b	14.9	75.8	-33.3	-27.7	31.5	89.7	5.3e+9	4.5e+3
TS4a	26.9	31.3	-21.1	-23.6	37.4	43.1	1.3e+9	3.2e+8
TS4b	23.5	30.7	-14.1	-19.9	30.5	40.7	6.7e+9	5.9e+8
TS5a	75.1	74.1	-31.0	-29.1	90.7	88.6	3.5e+3	5.7e+3
TS5b	11.9	74.9	-31.9	-28.5	27.9	89.2	1.3e+10	5.0e+3
TS6	67.0	71.3	-31.4	-32.6	82.7	87.5	2.4e+4	7.5e+3

Table S4. Activation parameters (enthalpy, entropy and free energy, rate constants) at 227°C determined by static DFT for type B isomerization reactions, in the forward (+ subscript) directions, lumped as a function of the branching degrees of the reactants and products. s = secondary cation, t = tertiary cation.

Branching degree of the reactant and products	Carbenium ion under consideration	k_{+} (s ⁻¹)	ΔH_{+}^{\ddagger} (kJ/mol)	ΔS_{+}^{\ddagger} (J/mol/K)	ΔG_{+}^{\ddagger} (kJ/mol)	Average under consideration
Linear \rightarrow Monobranched	s \rightarrow s	2.4e+9	24.3	-21.9	35.2	TS1a, TS1b, TS2
Monobranched \rightarrow Dibranched	s \rightarrow s	4.1e+9	25.2	-17.6	34.0	TS4a, TS4b
	s \rightarrow t	9.2e+9	13.4	-32.6	29.7	TS3b, TS5b
Dibranched \rightarrow Tribranched	t \rightarrow t	7.6e+3	69.0	-38.3	88.2	TS3a, TS5a
	t \rightarrow t	2.4e+4	67.0	-31.4	82.7	TS6

The reader is referred to the nomenclature presented at the end of the present document for the meaning of each term in equations. We consider that adsorption and desorption processes are very fast so that equilibrium can be considered. In the ideal hydrocracking process, the hydrogenation / dehydrogenation reactions on the metallic phase are very fast and thermodynamic equilibrium can also be assumed. Therefore, thermodynamic equilibrium is achieved in the gas phase between the paraffins and the corresponding olefins (as illustrated in equation (1), the reference pressure being equal to 1 atm.).

$$K_{DH,g}^{P_i} = \frac{\frac{P_{O_i} \cdot P_{H_2}}{P_o \cdot P_o}}{\frac{P_{P_i}}{P_o}} = \frac{P_{H_2} \cdot P_{O_i}}{P_{P_i} \cdot P_o} \quad (1)$$

In the ideal hydrocracking process, the rate determining steps take place on the acidic phase of the catalyst (zeolite). However, some reversible reactions on the acidic phase are faster than others and can also be considered at thermodynamic equilibrium. This is the case, for the adsorption and desorption of olefins (equation (2)) in zeolite and protonation / deprotonation reactions (equation (3)).

$$K_{ads}^{O_i} = \frac{\theta_{O_i,A}}{\frac{P_{O_i}}{P_o} \cdot \theta_{H^+,A}} \quad (2)$$

$$K_{Pr}^{O_i} = \frac{\theta_{R_i^+,A}}{\theta_{O_i,A}} \quad (3)$$

The molar fraction of adsorbed carbenium ions on the acidic sites is expressed as follows:

$$\theta_{R_i^+,A} = K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}} \cdot \theta_{H^+,A} \quad (4)$$

The molar fraction of adsorbed olefins on the acidic sites is obtained combining equations (2) and (3).

$$\theta_{O_i,A} = K_{ads}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}} \cdot \theta_{H^+,A} \quad (5)$$

The conservation of the overall acidic sites (equation (6)) leads to the determination of the molar fraction of free acidic sites (equation (7)).

$$1 = \theta_{H^+,A} + \sum_i \theta_{R_i^+,A} + \sum_j \theta_{O_j,A} \quad (6)$$

$$\theta_{H^+,A} = \frac{1}{1 + \sum_j K_{ads}^{O_j} \cdot K_{DH,g}^{P_j} \cdot \frac{P_{P_j}}{P_{H_2}} + \sum_i K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}} \quad (7)$$

Therefore, the molar fraction of adsorbed carbenium ions on the acidic sites can be determined from the partial pressures of the corresponding paraffins in the gas phase (equation (8)).

$$\theta_{R_i^+,A} = \frac{K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}}{1 + \sum_j K_{ads}^{O_j} \cdot K_{DH,g}^{P_j} \cdot \frac{P_{P_j}}{P_{H_2}} + \sum_i K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}} \quad (8)$$

The PCP isomerization of a carbenium ion is a reversible elementary rate determining step. The kinetic rate expressions of the forward and reverse reactions are given in equations (9) and (10).

$$r_{isom}^+ = k_{isom}^+ \cdot \theta_{R_i^+,A} \quad (9)$$

$$r_{isom}^- = k_{isom}^- \cdot \theta_{iR_i^+,A} \quad (10)$$

Those kinetic rates can be expressed as a function of paraffin partial pressures in the gas phase combining equations (8), (9) and (10).

$$r_{isom}^+ = \frac{k_{isom}^+ \cdot K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}}{1 + \sum_j K_{ads}^{O_j} \cdot K_{DH,g}^{P_j} \cdot \frac{P_{P_j}}{P_{H_2}} + \sum_i K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}} \quad (11)$$

$$r_{isom}^- = \frac{k_{isom}^- \cdot K_{ads}^{iO_i} \cdot K_{Pr}^{iO_i} \cdot K_{DH,g}^{iP_i} \cdot \frac{P_{iP_i}}{P_{H_2}}}{1 + \sum_j K_{ads}^{O_j} \cdot K_{DH,g}^{P_j} \cdot \frac{P_{P_j}}{P_{H_2}} + \sum_i K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}} \quad (12)$$

The same method is applied with the cracking reactions (no reversibility in this case).

$$r_{crack} = k_{crack} \cdot \theta_{R_1^+,A} \quad (13)$$

The kinetic rate can be expressed as a function of paraffin partial pressures in the gas phase combining equations (8) and (13).

$$r_{crack} = \frac{k_{crack} \cdot K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}}{1 + \sum_j K_{ads}^{O_j} \cdot K_{DH,g}^{P_j} \cdot \frac{P_{P_j}}{P_{H_2}} + \sum_i K_{ads}^{O_i} \cdot K_{Pr}^{O_i} \cdot K_{DH,g}^{P_i} \cdot \frac{P_{P_i}}{P_{H_2}}} \quad (14)$$

The kinetic constants depend essentially on the type of the carbenium ions involved (s: secondary, t: tertiary).⁵ This was also confirmed by ab initio calculations. Therefore, there are only four independent kinetic constants for isomerization reactions and four independent kinetic constants for cracking reactions:

$$k_{isom(s,s)}, k_{isom(s,t)}, k_{isom(t,s)}, k_{isom(t,t)} \\ k_{crack(s,s)}, k_{crack(s,t)}, k_{crack(t,s)}, k_{crack(t,t)}$$

Ab initio calculations is a way to estimate those constants as well as the olefin adsorption / desorption constants and the protonation / deprotonation equilibrium constants. The only unknowns in the kinetic rate law expressions (equations (11), (12), (14)) are the gas phase equilibrium constants of dehydrogenation / hydrogenation of paraffins.

In the context of the n-heptane hydrocracking, paraffins involved in the reaction network are well known and their thermodynamic characteristics are tabulated. To estimate these equilibrium constants, a Benson group contribution method was used.⁶ This method is very reliable for such simple molecules. It consists in calculating their standard enthalpies and the entropies of formation as well as their molar heat capacities as a function of temperature (3rd degree polynomial).

$$C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^3 \quad (15)$$

The equilibrium constants are determined from the reaction Gibbs free energies.

$$K_i = e^{-\frac{\Delta G_i^g}{R \cdot T}} \quad (16)$$

The Gibbs free energy is expressed as a function of the reaction enthalpy and entropy.

$$\Delta G_i^g = \Delta H_i^g - T \cdot \Delta S_i^g \quad (17)$$

However, all these quantities depend on the temperature and are expressed as a function of their value under standard conditions (1 atmosphere, 25 °C.) and of the molar heat capacities of the compounds involved in the considered reaction.

$$\Delta H_i^g = (\Delta H_{prod,f}^g - \Delta H_{reac,f}^g) + \int_{298.15}^T (\Delta a + \Delta b \cdot T + \Delta c \cdot T^2 + \Delta d \cdot T^3) \cdot dT \quad (18)$$

$$\Delta S_i^g = (\Delta S_{prod,f}^g - \Delta S_{reac,f}^g) + \int_{298.15}^T \left(\frac{\Delta a}{T} + \Delta b + \Delta c \cdot T + \Delta d \cdot T^2 \right) \cdot dT \quad (19)$$

Isomerization reactions without changing in the number of branches are very fast.⁷ Therefore, paraffins characterized by the same number of carbon atoms and the same number of branches can be considered at thermodynamic equilibrium. One can thus define the following groups for isomers:

- Linear paraffins
- Mono-branched paraffins
- Di-branched paraffins
- Tri-branched paraffins

Since only PCP isomerization reactions are taken into account, the micro-kinetic model will not be able to respect those thermodynamic constraints within groups. To address this problem, it is necessary, during the integration along the reactor height, to rebalance the isomers of the groups so that the concentrations of the carbenium ions are representative of the equilibrium. The thermodynamic equilibrium within a group is calculated by a Benson group contribution method.⁶ In the group of mono-branched paraffins, the paraffins involved are: 2-methylhexane (2MeC6), 3-methylhexane (3MeC6) and 3-ethylpentane (3EtC5). For this group, the equilibrium constants are defined below:

$$K_{1,m} = \frac{P_{2MeC6}}{P_{3MeC6}} \quad (20)$$

$$K_{2,m} = \frac{P_{3EtC5}}{P_{3MeC6}} \quad (21)$$

This results in the following molar compositions within the group of mono-branched paraffins:

$$x_{2MeC6} = \frac{K_{1,m}}{1+K_{1,m}+K_{2,m}} \quad (22)$$

$$x_{3MeC6} = \frac{1}{1+K_{1,m}+K_{2,m}} \quad (23)$$

$$x_{3EtC5} = \frac{K_{2,m}}{1+K_{1,m}+K_{2,m}} \quad (24)$$

In the group of di-branched paraffins, the paraffins involved are: 2,2-dimethylpentane (22diMeC5), 2,3-dimethylpentane (23diMeC5), 2,4-dimethylpentane (24diMeC5) and 3,3-dimethylpentane (33diMeC5). For this group, the equilibrium constants are defined below. This results in the following molar compositions within the group of di-branched paraffins:

$$x_{22diMeC5} = \frac{1}{1+K_{1,d}+K_{2,d}+K_{3,d}} \quad (25)$$

$$x_{23diMeC5} = \frac{K_{1,d}}{1+K_{1,d}+K_{2,d}+K_{3,d}} \quad (26)$$

$$x_{24diMeC5} = \frac{K_{2,d}}{1+K_{1,d}+K_{2,d}+K_{3,d}} \quad (27)$$

$$x_{33diMeC5} = \frac{K_{3,d}}{1+K_{1,d}+K_{2,d}+K_{3,d}} \quad (28)$$

For the group of tri-branched paraffins, there is no equilibrium calculation because there is only one isomer (2,2,3-trimethylbutane).

To summarize, 45 rate determining steps are taken into account:

- 40 PCP isomerization reactions decomposed into 26 secondary-secondary reactions (s-s), 4 secondary-tertiary reactions (s-t), 4 tertiary-secondary reactions (t-s) and 6 tertiary-tertiary reactions (t-t).
- 5 β scission reactions decomposed into 3 secondary-secondary reactions (s-s), 1 secondary-tertiary reaction (s-t), 1 tertiary-secondary reaction (t-s).

Nomenclature

a, b, c, d	Polynomial coefficient for molar heat capacity	[u.i]
C_{site}^A	Total concentration of acidic site in the zeolite	[mol/kg]
C_p	Molar heat capacity	[J/mol/K]
F_i^g	Molar flowrate of compound i in the gas phase	[mol/m ³]
h	Planck constant	[m ² /kg/s]
k	Kinetic constant	[s ⁻¹]
k_{crack}	Cracking kinetic constant	[s ⁻¹]
k_{isom}^+	Forward isomerization kinetic constant	[s ⁻¹]
k_{isom}^-	Reverse isomerization kinetic constant	[s ⁻¹]
$K_{ads}^{O_i}$	Adsorption equilibrium constant for olefin O_i	[-]
$K_{DH,g}^{P_i}$	Dehydrogenation / hydrogenation gas equilibrium constant for paraffin P_i	[-]
$K_{Pr}^{O_i}$	Protonation / deprotonation equilibrium Constant for olefin O_i	[-]
$K_{1,m}$	Equilibrium constant between 2Me C ₆ and 3Me C ₆	[-]
$K_{2,m}$	Equilibrium constant between 3Et C ₅ and 3Me C ₆	[-]
$K_{1,d}$	Equilibrium constant between 23diMe C ₅ and 22diMe C ₅	[-]
$K_{2,d}$	Equilibrium constant between 24diMe C ₅ and 22diMe C ₅	[-]
$K_{3,d}$	Equilibrium constant between 33diMe C ₅ and 22diMe C ₅	[-]
P_{H_2}	Hydrogen partial pressure	[Pa]
P_{O_i}	Olefin O_i partial pressure	[Pa]
P_0	Reference pressure	[Pa]
P_{P_i}	Paraffin P_i partial pressure	[Pa]
P_{3EtC5}	3Et C ₅ partial pressure	[Pa]
P_{2MeC6}	2Me C ₆ partial pressure	[Pa]
P_{3MeC6}	3Me C ₆ partial pressure	[Pa]
r_j	Reaction rate of reaction j	[s ⁻¹]
r_{crack}	Cracking reaction rate	[s ⁻¹]
r_{isom}^+	Forward reaction rate of isomerization	[s ⁻¹]
r_{isom}^-	Reverse reaction rate of isomerization	[s ⁻¹]
S_r	Reactor section	[m ²]
T	Temperature	[K]
x_{2MeC6}	2Me C ₆ molar fraction mono-branched paraffin group	[-]
x_{3MeC6}	3Me C ₆ molar fraction mono-branched paraffin group	[-]
x_{3EtC5}	3Et C ₅ molar fraction mono-branched paraffin group	[-]
$x_{22diMeC5}$	22diMe C ₅ molar fraction di-branched paraffin group	[-]
$x_{23diMeC5}$	23diMe C ₅ molar fraction di-branched paraffin group	[-]
$x_{24diMeC5}$	24diMe C ₅ molar fraction di-branched paraffin group	[-]
$x_{33diMeC5}$	33diMe C ₅ molar fraction di-branched paraffin group	[-]

z	Axial position in the reactor	[m]
Greek symbols		
$\Delta a, \Delta b, \Delta c, \Delta d$	Coefficient differences between products and reactants	[u.i]
ε_s	Solid holdup	[-]
$\Delta H_{prod,f}^g$	Product standard enthalpy of formation	[J/mol]
$\Delta H_{reac,f}^g$	Reactant standard enthalpy of formation	[J/mol]
$\Delta S_{prod,f}^g$	Product standard entropy of formation	[J/mol/K]
$\Delta S_{reac,f}^g$	Reactant standard entropy of formation	[J/mol/K]
ΔG_i^g	i^{th} Reaction Gibbs free energy	[J/mol]
ΔH_i^g	i^{th} Reaction enthalpy	[J/mol]
ΔS_i^g	i^{th} Reaction entropy	[J/mol/K]
$\Delta H^\#$	Activation enthalpy	[J/mol]
$\Delta S^\#$	Activation entropy	[J/mol/K]
ρ_s	Solid grain density	[kg/m ³]
$\theta_{H^+,A}$	Molar ratio of free acidic sites H^+	[-]
$\theta_{O_i,A}$	Molar ratio of olefin O_i adsorbed on acidic sites	[-]
$\theta_{R_i^+,A}$	Molar ratio of carbenium ion R_i^+ adsorbed on acidic sites	[-]
$\theta_{iR_i^+,A}$	Molar ratio of carbenium ion iR_i^+ issued from isomerization of R_i^+	[-]
μ_{ij}	Stoichiometric coefficients of compound i in reaction j	[-]

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