Supporting Information

Influence of Nanoscale Intimacy and Zeolite Micropore Size on the Performance of Bifunctional Catalysts for *n*-Heptane Hydroisomerization

Jogchum Oenema[†], *Justine Harmel*[†], *Roxana Pérez Vélez*[†], *Mark J. Meijerink*[†], *Willem Eijsvogel*[†], *Ali Poursaeidesfahani*[‡], *Thijs J.H. Vlugt*[‡], *Jovana Zečević*[†], *Krijn P. de Jong*[*,†]

† Inorganic Chemistry and Catalysis, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands.

‡ Process & Energy Department, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands.

*E-mail: k.p.dejong@uu.nl

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Supporting Information 1

n-C_7 conversion ($X_{n\text{-}C7}$) was calculated by:

$$X_{n\text{-}C_7} = \left(1 - \frac{F_{C\ wt.\ n\text{-}C_7,out}}{F_{C\ wt.\ n\text{-}C_7,in}}\right) \cdot 100\%$$

Wherein $F_{C\ wt.\ n\text{-}C_7,out}$ and $F_{C\ wt.\ n\text{-}C_7,in}$ are the flows, based on weight of carbon, of *n*-C_7 going out or into the reactor, respectively.

C_7 isomer yield ($Y_{i\text{-}C_7}$) was calculated by:

$$Y_{i\text{-}C_7} = \left(\frac{F_{C\ wt.\ i\text{-}C_7,out}}{F_{C\ wt.\ n\text{-}C_7,in}}\right) \cdot 100\%$$

The yield of cracked products ($Y_{C_3+C_4}$) was calculated by:

$$Y_{C_3+C_4} = \left(\frac{F_{C\ wt.\ C_3,out} + F_{C\ wt.\ C_4,out}}{F_{C\ wt.\ n\text{-}C_7,in}}\right) \cdot 100\%$$

Wherein $F_{C\ wt.\ i\text{-}C_7,out}$ and $F_{C\ wt.\ C_m,out}$ are the flows, based on weight of carbon, of *i*-C_7 or cracked products C_m (m = 1-6), respectively, going out of the reactor.

The *i*-C_7 isomer selectivity ($S_{i\text{-}C_7}$) was determined as follows:

$$S_{i\text{-}C_7} = \left(\frac{F_{C\ wt.\ i\text{-}C_7,out}}{F_{C\ wt.\ n\text{-}C_7,in} - F_{C\ wt.\ n\text{-}C_7,out}}\right) \cdot 100\%$$

The selectivity towards cracked products (S_{C_m}) was determined as follows:

$$S_{C_m} = \left(\frac{F_{C\ wt.\ C_m,out}}{F_{C\ wt.\ n\text{-}C_7,in} - F_{C\ wt.\ n\text{-}C_7,out}}\right) \cdot 100\%$$

Table S1. Details of the parent zeolites.

	Zeolite Code[a]	Si/Al Zeolite[a] ($at \cdot at^{-1}$)	Ring size[b]	Micropore size (nm)[b]	Micropore tortuosity[b]	Estimated particle size (nm)[c]
ZSM-5	CBV3024E	15	10	0.55 × 0.51 + 0.56 × 0.53	Straight + Sinusoidal	20-200
Zeolite Beta	CP814E	12.5	12	0.66 × 0.67 + 0.56 × 0.56	Straight pores	20-50
Zeolite Y	CBV760	30	12	0.74 × 0.74	Straight pores + cages	200-1000

a) Manufacturers specification, Zeolyst.
b) International Zeolite Association (Ch. Baerlocher, L.B. McCusker; Database of Zeolite Structures)
c) Obtained from TEM analysis

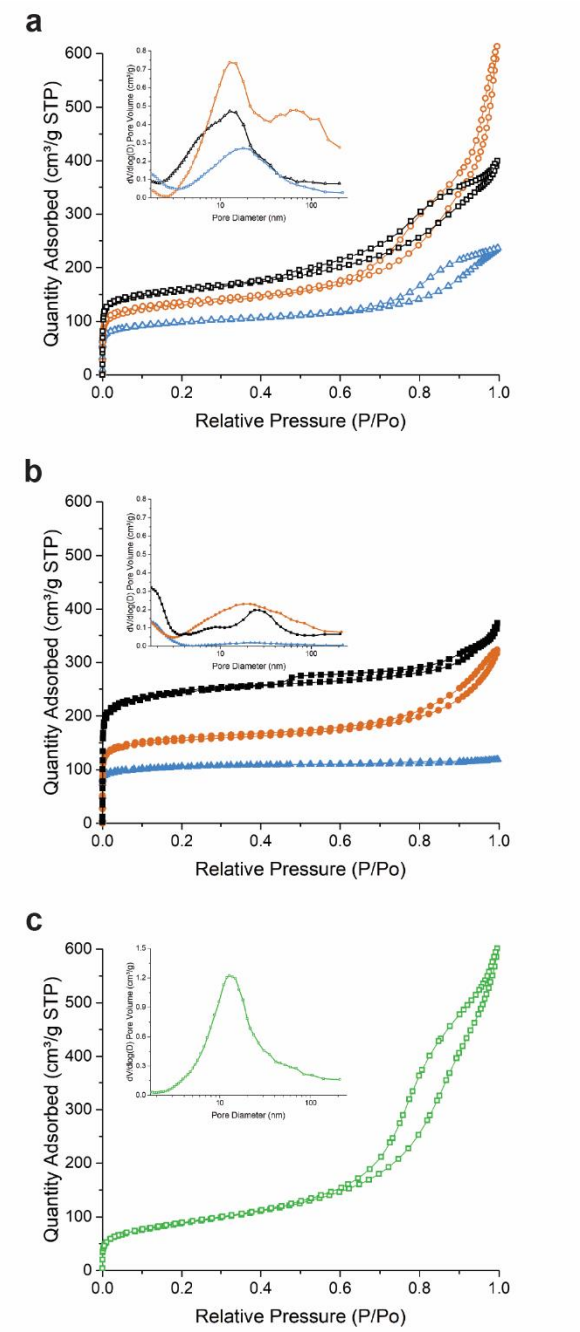

Figure S1. N_2 physisorption isotherms of the Zeolite/γ- Al_2O_3 (50/50 wt.) composites, with the BJH pore size distributions derived from the adsorption branch as insert (a): ZSM-5/γ- Al_2O_3 composite (blue), Zeolite Beta/γ-Al_2O_3 composite (orange) and Zeolite Y/γ- Al_2O_3 (black). Parent zeolites (b): ZSM-5 (blue), Zeolite Beta (orange) and Zeolite Y (black) and the γ- Al_2O_3 binder (c).

Table S2. Quantitative information derived from N_2 physisorption measurements.

Sample	BET surface area ($m^2 \cdot g^{-1}$)	t-plot external surface area ($m^2 \cdot g^{-1}$)	t-plot micropore volume ($cm^3 \cdot g^{-1}$)	BJH mesopore volume ($cm^3 \cdot g^{-1}$)
ZSM-5/γ- Al_2O_3	-	135	0.09	0.26
Zeolite Beta/γ- Al_2O_3	-	187	0.12	0.80
Zeolite Y/ γ- Al_2O_3	-	209	0.15	0.47
ZSM-5	-	77	0.13	0.04
Zeolite Beta	-	135	0.18	0.30
Zeolite Y	-	231	0.28	0.24
γ- Al_2O_3	314	-	-	0.89

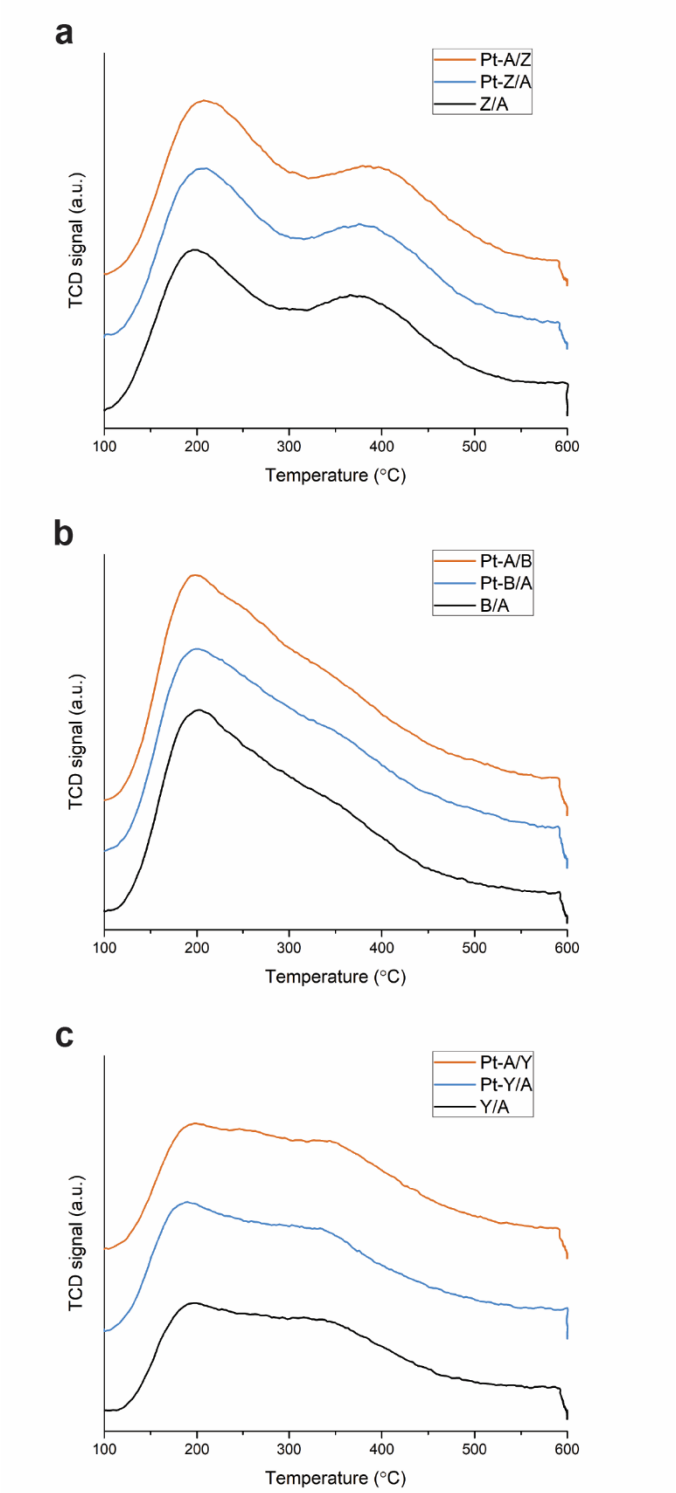

Figure S2. NH_3-TPD profiles of the Pt/γ- Al_2O_3/zeolite composite catalysts and the zeolite/γ- Al_2O_3 composite support. Catalysts or supports are based on ZSM-5 (a), zeolite Beta (b), and Zeolite Y (c).

Table S3. Total acidity of Pt/γ- Al_2O_3/zeolite composite catalysts and zeolite/γ- Al_2O_3 composite supports as obtained by NH_3-TPD.

Sample	Total NH_3 desorped ($mmol \cdot g^{-1}$)
Pt-A/Z	0.79
Pt-Z/A	0.75
Z/A (ZSM-5/γ- Al_2O_3)	0.70
Pt-A/B	0.75
Pt-B/A	0.72
B/A (Zeolite Beta/γ- Al_2O_3)	0.64
Pt-A/Y	0.54
Pt-Y/A	0.51
Y/A (Zeolite Y/γ- Al_2O_3)	0.41

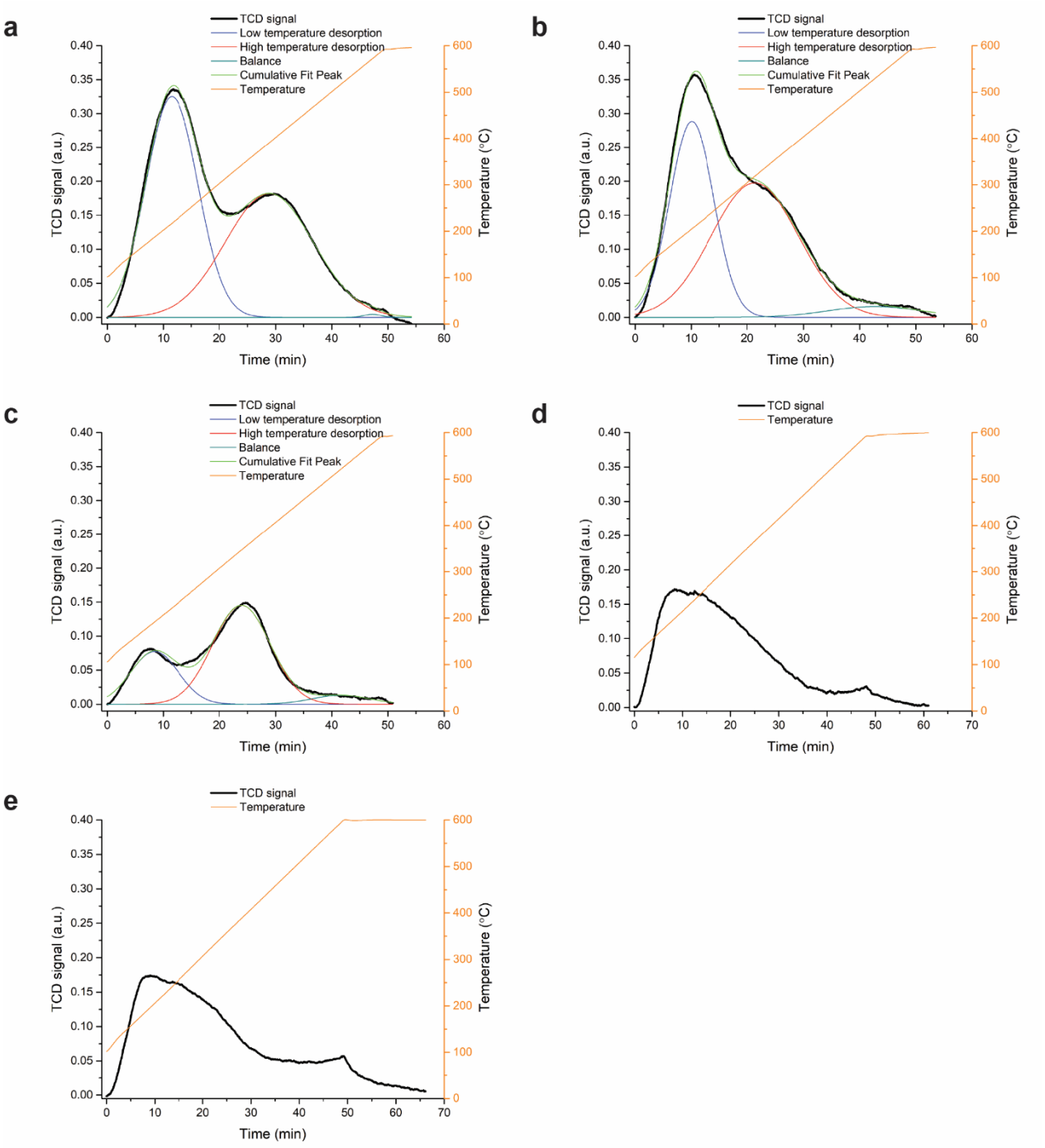

Figure S3. NH_3-TPD profiles of parent ZSM-5 (a), zeolite Beta (b), zeolite Y (c) γ-Al_2O_3 (d) and γ-Al_2O_3 that was peptized with acetic acid prior to calcination (e).

Table S4. Results of deconvolution low temperature and high temperature desorption of the NH_3-TPD signal of parent zeolites. The total acidity is calculated by integration of the TCD signal over the temperature range of 100-600˚C.

	Si/Al Zeolite	NH_3 desorbed Low temperature ($mmol_{NH3} \cdot g_{cat}^{-1}$)	NH_3 desorbed High temperature ($mmol_{NH3} \cdot g_{cat}^{-1}$)	Total NH_3 desorbed ($mmol_{NH3} \cdot g_{cat}^{-1}$)
ZSM-5	15	0.42	0.40	0.82
Zeolite Beta	12.5	0.31	0.42	0.73
Zeolite Y	30	0.09	0.21	0.32
γ-Al_2O_3	-	-	-	0.49
γ-Al_2O_3 (peptized)	-	-	-	0.56

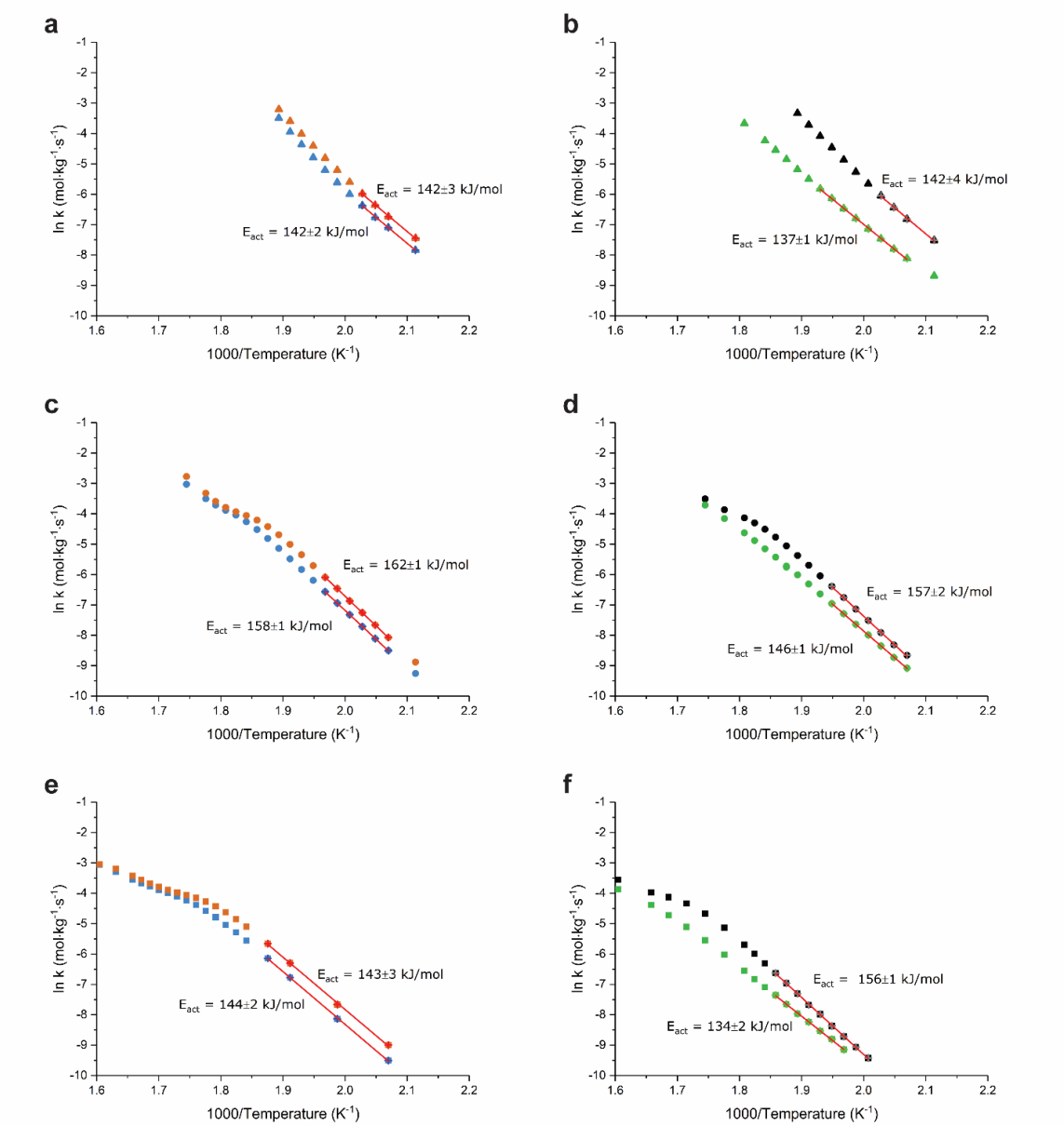

Figure S4. Arrhenius plots for ZSM-5 (a, b), Zeolite Beta (c, d) and Zeolite Y (e, f) based catalysts, at a feedrate of 2.6 $g_{n\text{-}C7} \cdot g_{cat} \cdot h^{-1}$, 10 bar of total pressure and 9 $mol_{H2}/mol_{n\text{-}C7}$. Catalyst with closest intimacy between Pt sites and zeolite sites are indicated in blue, catalyst with a nanoscale intimacy are indicated in orange, intimate physical mixtures are indicated in black while physical mixtures of grains are indicated in green. The indicated errors of the apparent activation energies denote the standard error of the fit. The first order rate constant was obtained from $ln(k) = ln\left(-\frac{ln(1-X)}{W/F}\right)$ wherein X is the *n*-C_7 conversion, W the catalyst mass (kg) and F the molar flow of *n*-heptane ($mol \cdot s^{-1}$). Datapoints at relatively low conversion levels were fitted to a straight line, and the slope of this line was then multiplied by -R (gasconstant, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$) to obtain the apparent activation energy. Previous kinetic studies by Guisnet et al. (Appl. Catal. 71 (1991) 295–306) and Van de Runstraat et al. (J. Catal. 171 (1997) 77–84) have confirmed that a first order dependence of relatively light hydrocarbons in hydro-isomerization is a valid assumption.

Table S5. Pre-exponential factors and apparent activation energies of Pt/γ- Al_2O_3/zeolite composite catalysts and physical mixtures. The indicated errors of the activation energy denote the standard error of the fit.

	Pre-exponential factor ($mol \cdot kg^{-1} \cdot s^{-1}$)	Apparent activation energy ($kJ \cdot mol^{-1}$)
Pt-Z/A	$1.7 \cdot 10^{12}$	142 ± 2
Pt-A/Z	$2.7 \cdot 10^{12}$	142 ± 3
Intimate phys. mix. (ZSM-5)	$2.6 \cdot 10^{12}$	142 ± 4
Phys. mix. grains (ZSM-5)	$2.0 \cdot 10^{11}$	137 ± 1
Pt-B/A	$2.6 \cdot 10^{13}$	158 ± 1
Pt-A/B	$1.1 \cdot 10^{14}$	162 ± 1
Intimate phys. mix. (Zeolite Beta)	$1.7 \cdot 10^{13}$	157 ± 2
Phys. mix. grains (Zeolite Beta)	$7.7 \cdot 10^{11}$	146 ± 1
Pt-Y/A	$2.9 \cdot 10^{11}$	144 ± 2
Pt-A/Y	$3.8 \cdot 10^{11}$	143 ± 3
Intimate phys. mix. (Zeolite Y)	$1.8 \cdot 10^{12}$	156 ± 1
Phys. mix. grains (Zeolite Y)	$5.9 \cdot 10^{9}$	134 ± 2

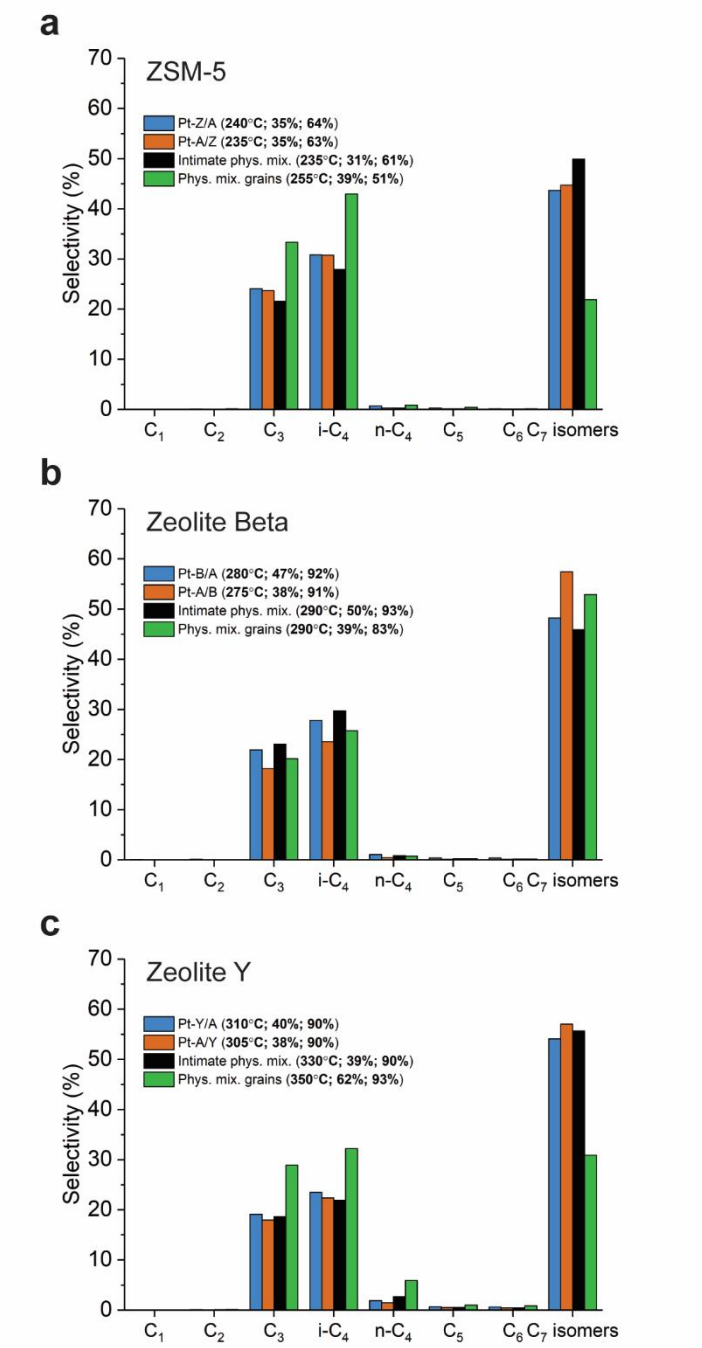

Figure S5. The cracking products distribution pattern for the ZSM-5 based catalysts (a), zeolite Beta based catalysts (b) and zeolite Y based catalyst (c). Data between brackets denote: reactor temperature; cracking conversion; total *n*-heptane conversion, respectively.

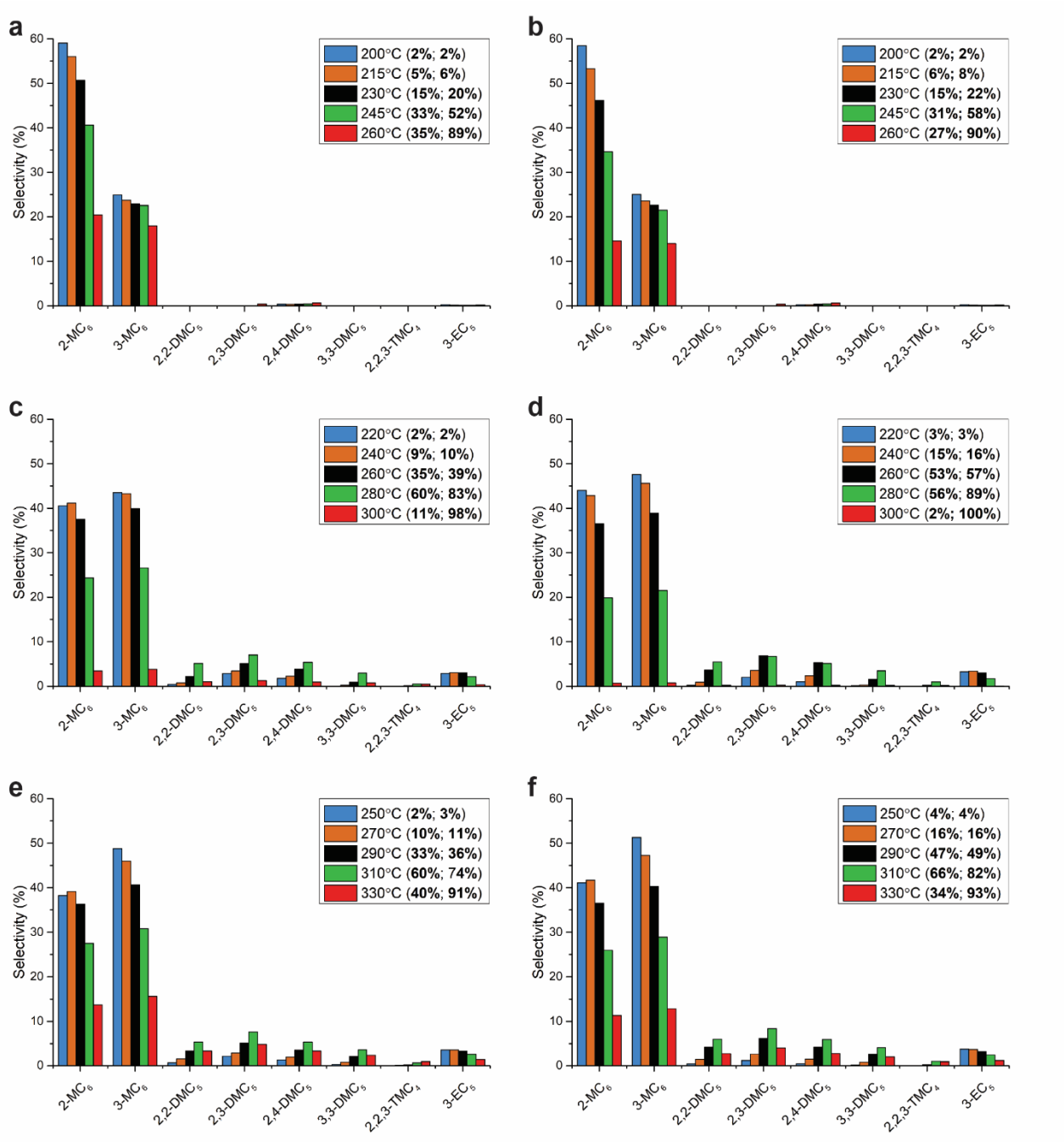

Figure S6. Isomer product distribution ZSM-5 (a,b), Zeolite Beta (c,d) and Zeolite Y (e,f) at a feedrate of 2.6 $g_{n\text{-}C7} \cdot g_{cat} \cdot h^{-1}$ and 10 bar of total pressure. Data between brackets denote: isomer yield; total *n*-heptane conversion, respectively.

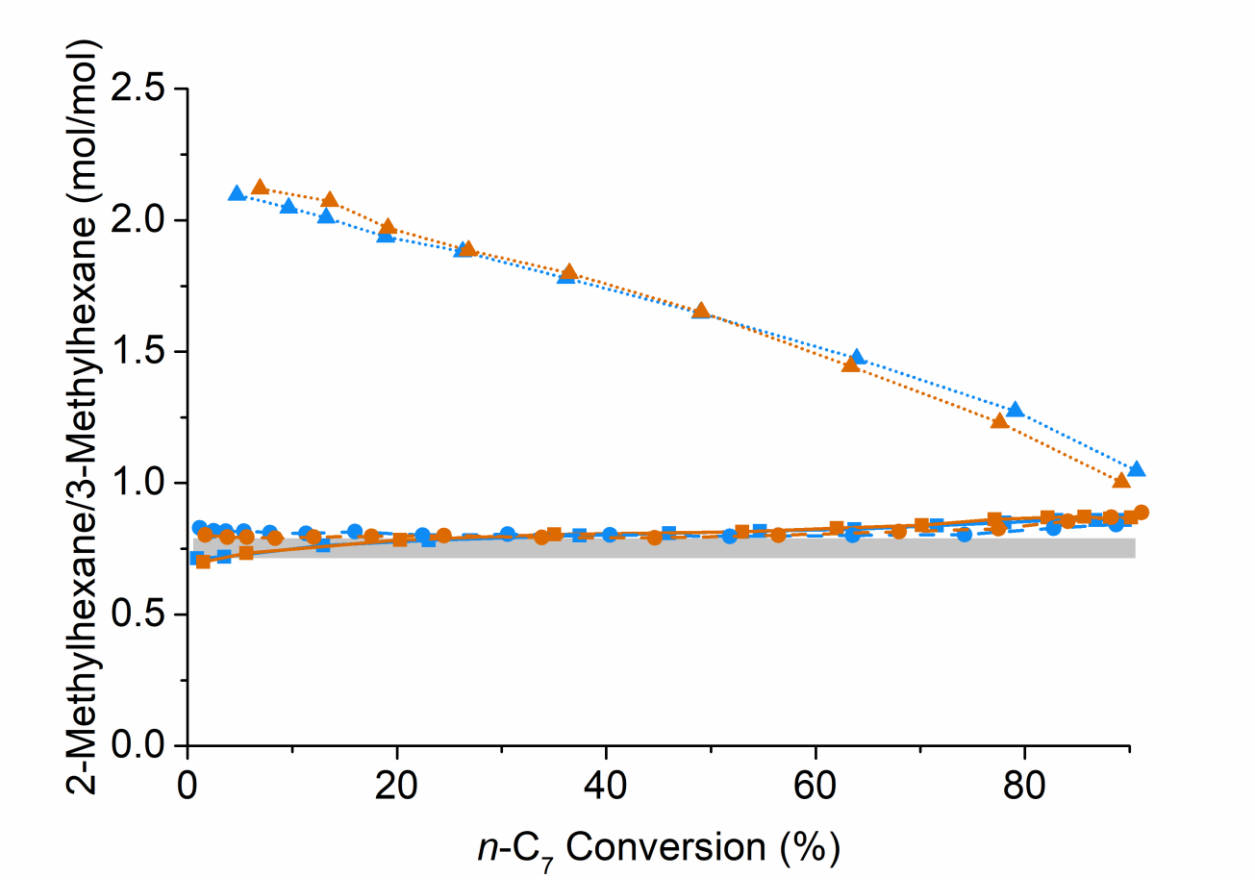

Figure S7. Ratio between 2-Methylhexane and 3-Methylhexane as a function of conversion for ZSM-5 (triangles), zeolite Beta (circles) and zeolite Y (squares). Catalyst with Pt nanoparticles located in the zeolite are indicated in blue, while catalyst with Pt nanoparticles located on the γ-Al_2O_3 binder indicated in orange. The grey rectangle indicates the value (2-Methylhexane/[(*R*)-3-Methylhexane + (*S*)-3-Methylhexane]) at thermodynamic equilibrium between 200-300˚C as was computed with Outotec HSC Chemistry software, v9.

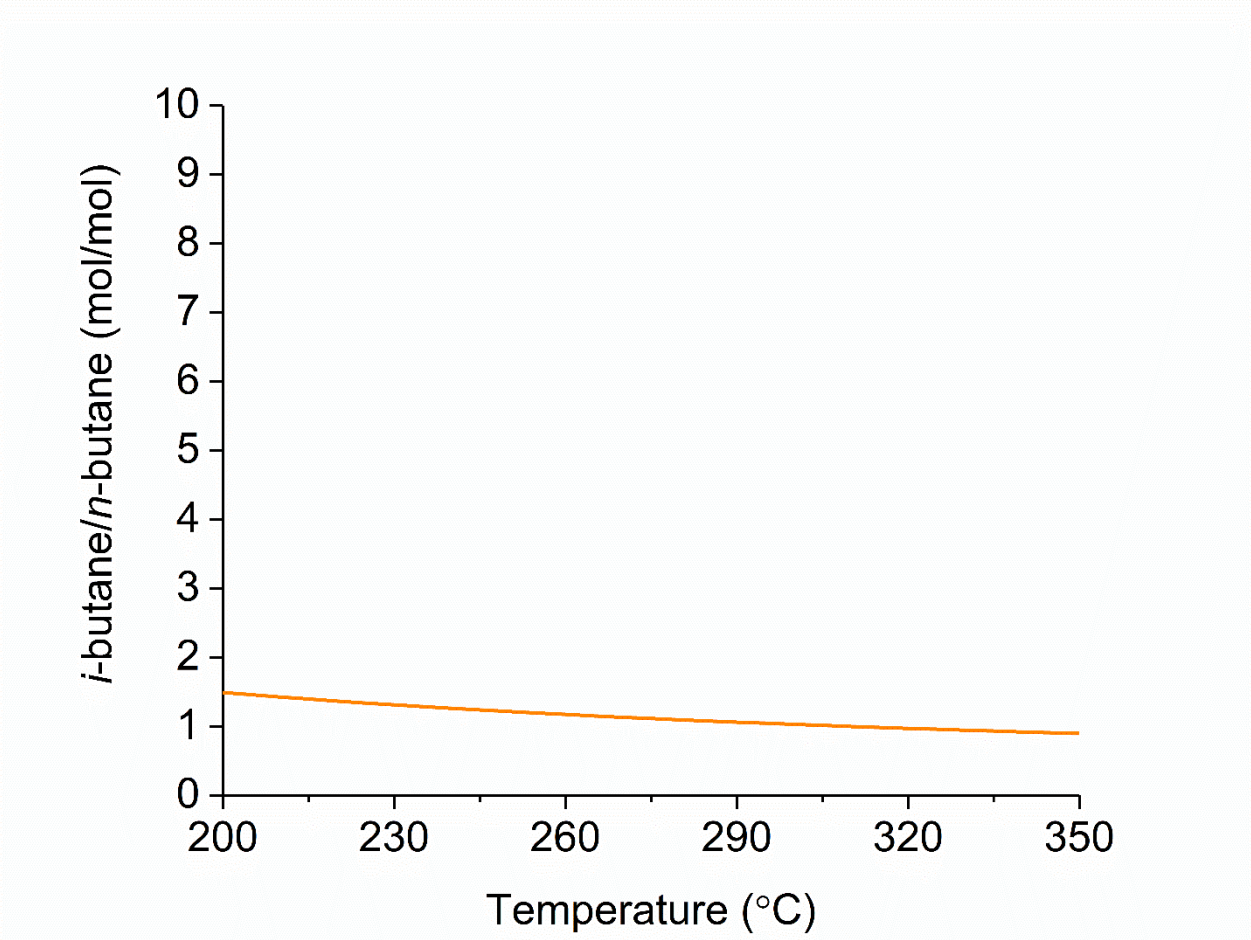

Figure S8: Ratio between *i*-butane and *n*-butane (mol/mol) at thermodynamic equilibrium between 200 and 350 °C. The value was computed with Outotec HSC Chemistry software, v9.

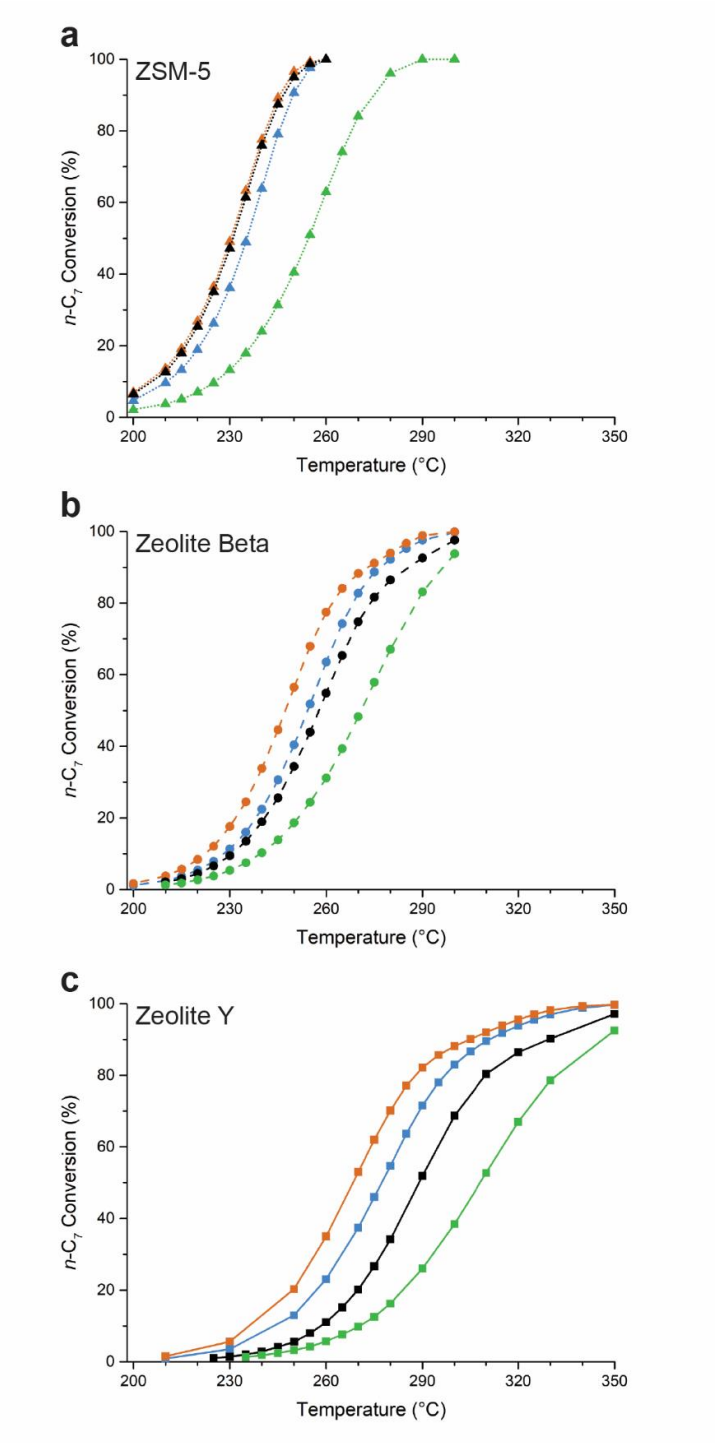

Figure S9. Conversion of *n*-heptane as a function of temperature of ZSM-5 (a), Zeolite Beta (b) and Zeolite Y (c) at a feedrate of 2.6 $g_{n\text{-}C7} \cdot g_{cat} \cdot h^{-1}$ at 10 bar of total pressure and 9 $mol_{H2}/mol_{n\text{-}C7}$. Catalyst with closest intimacy between Pt sites and zeolite sites are indicated in blue, catalyst with a nanoscale intimacy are indicated in orange, intimate physical mixtures are indicated in black while physical mixtures of grains are indicated in green.