

## Appendix A: Preparation of zeolites

NH<sub>4</sub>-BEA zeolite was calcined to obtain the protonic form using a protocol published elsewhere (J.P. Marques et al., Chem. Commun. (2004) 2290–2291).

The parent hydrogel for NU-10 was prepared by stirring, firstly, 18 g of colloid silica (40 wt.% SiO<sub>2</sub>) with 80 g of H<sub>2</sub>O during 2 min and adding, secondly, 1.1 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O, 1.9 g of K<sub>2</sub>O·H<sub>2</sub>O and 4.2 g of 1,6-diaminohexane. The hydrogel was stirred over 4 h at RT and over 2 days at 433 K. At the end of crystallisation period, the suspension was cooled to RT and filtered. The recovered solid was washed and dried at 373 K over 12 h. The sample was calcined under an air flow of 2 L h<sup>-1</sup> g<sup>-1</sup> to remove the organic template. The temperature was increased at a 1 K min<sup>-1</sup> rate and kept at 473 K over 2 h. After, an heating rate of 2 K min<sup>-1</sup> was used to reach 823 K and the plateau was hold over 12 h..

The parent hydrogel for EU-1 was prepared by stirring the Al source solution and Si source suspensions over 20 min. The Al source solution consisted of 0.30 g of NaAlO<sub>2</sub>, 1.1 g of NaOH and 27 g of H<sub>2</sub>O stirred till complete dissolution of the initial salts. The Si source suspension consisted of 15 g of colloid silica (40 wt.% SiO<sub>2</sub>), 29 g of hexamethonium bromide hydrate (58 wt.% H<sub>2</sub>O) and 27 g of H<sub>2</sub>O stirred during 15 min. After the initial mixing period of the hydrogel, stirring proceeded over 4 days at 453 K. At the end of crystallisation period, the suspension was cooled to RT and filtered. The recovered solid was washed and dried at 373 K over 12 h. The sample was calcined under an air flow of 2 L h<sup>-1</sup> g<sup>-1</sup> to remove the organic template. Four plateaux at 423, 523, 623 and 723 K over 1 h each and a final plateau at 823 K over 20h were performed. A heating rate of 5 K min<sup>-1</sup> was used to reach the first plateau. For the following plateaux 1 K min<sup>-1</sup> was used.

The parent hydrogel for ZSM-48 was prepared by stirring the Al source and Si source solutions over 30 min. The Al source solution consisted of 4.2 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 77 g of H<sub>2</sub>O stirred till complete dissolution of Al salt. The Si source suspension was prepared in three steps. Firstly 0.30 g of NaOH were dissolved in 121 g of sodium silicate solution (27 wt.% SiO<sub>2</sub>). After, 176 g of H<sub>2</sub>O and 13 g of H<sub>2</sub>SO<sub>4</sub> (95 wt% purity) were added and the solution was vigorously stirred over 2 h. Finally, 26 g of tetramethylammonium bromide, 233 g of H<sub>2</sub>O and 112 g of *n*-octylamine were added. After the initial mixing period of the hydrogel, stirring proceeded over 6 days at 433 K. At the end of this period, the suspension was cooled to RT and filtered. The recovered solid was washed and dried at 373 K over 64 h.

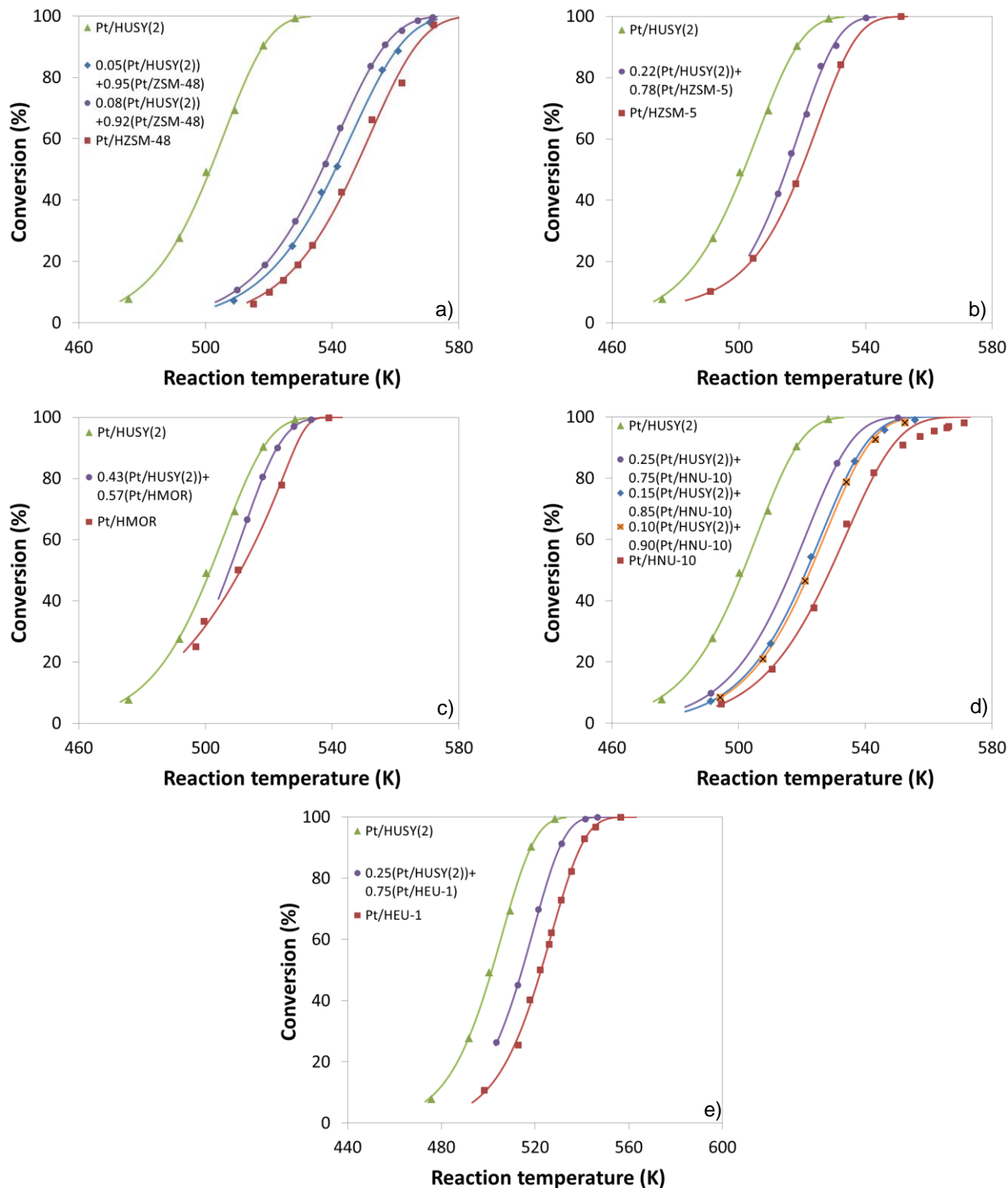
The sample was calcined under an air flow of  $2 \text{ L h}^{-1} \text{ g}^{-1}$  to remove the organic template. The temperature was increased at a  $1 \text{ K min}^{-1}$  rate and kept at 473 K over 2 h. After, an heating rate of  $2 \text{ K min}^{-1}$  was used to reach 823 K and the plateau was hold over 12 h.

EU-1, NU-10 and ZSM-48 zeolites were exchanged with  $\text{NH}_4^+$  to remove residual  $\text{Na}^+$  and  $\text{K}^+$  ions. The samples were stirred in a solution of  $\text{NH}_4\text{NO}_3$  (10 N), using a V/W (volume of solution (ml)/weight of dried catalyst (g)) ratio of 10. The slurry was heated under agitation at reflux temperature for 4 h and then centrifuged and washed. Samples were dried overnight at 353 K. The procedure was repeated twice in order to guarantee high cation exchange levels. For ZSM-48 (2), a V/P ratio of 20 is used as an initial value of 10 was insufficient to obtain a proper suspension of the powder. In order to obtain the solids in protonic form, the samples were calcined under air flow ( $2 \text{ L h}^{-1} \text{ g}^{-1}$ ) after drying at 383 K over 12 h. Three plateaux at 423, 523 and 623 over 1 h each and a final plateau at 823 K over 4h were performed. A heating rate of  $5 \text{ K min}^{-1}$  was used. Ion exchange efficiencies were superior to 90% issuing metal ion contents lower than 500 ppm.

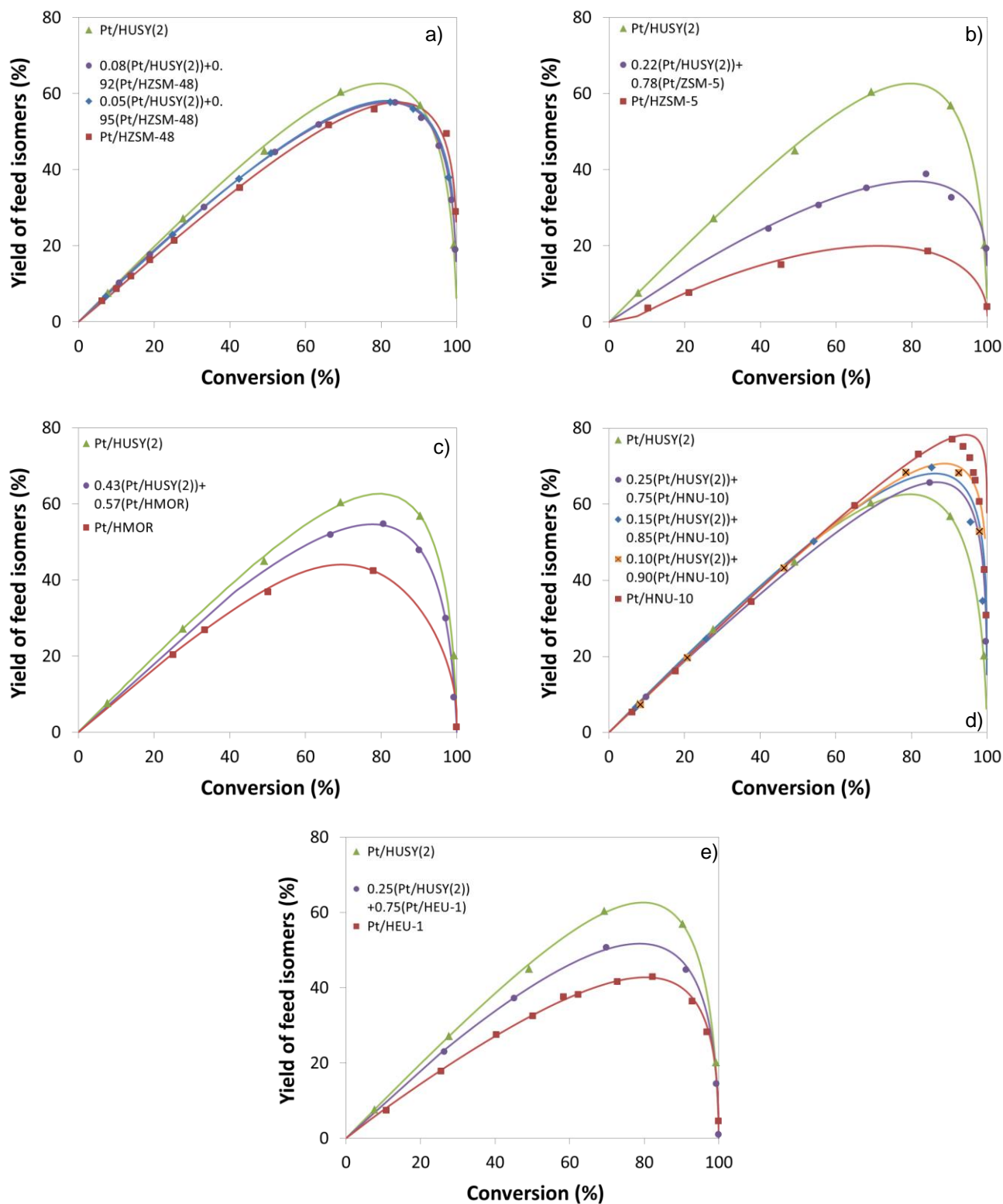
The structures of zeolites were confirmed by X-Ray Powder Diffraction evidencing as well high levels of crystallinity.

## Appendix B: Fitting of experimental results with the macrokinetic model

### Mixtures of Pt/HUSY(2) and Pt/zeolite catalysts



**Figure B.1:**  $n\text{-C}_{16}$  conversion as function of reaction temperature for Pt/HUSY(2) and Pt/zeolite catalysts. Symbols stand for experimental data and lines for model fitting results.

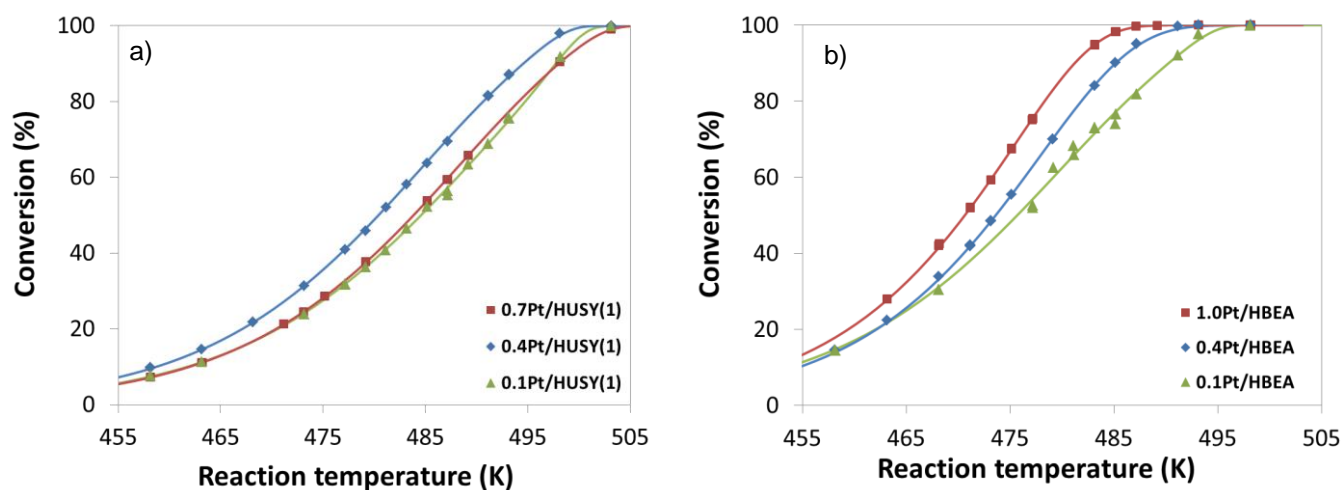


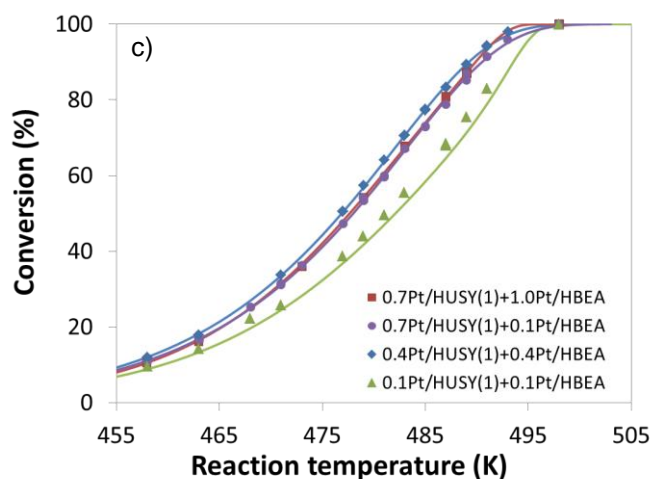
**Figure B.2:** Yield of C<sub>16</sub> isomers as function of conversion for a) Pt/HUSY(1), b) Pt/HBEA and c) Pt/HUSY(1) +Pt/HBEA.

**Table B.1:** Temperature at 50% feed conversion, turnover frequency over protonic sites at 490K and 513K, and maximum isomer yield for individual catalysts and hybrid catalysts based on Pt/HUSY(2) and Pt/zeolite catalysts mixtures

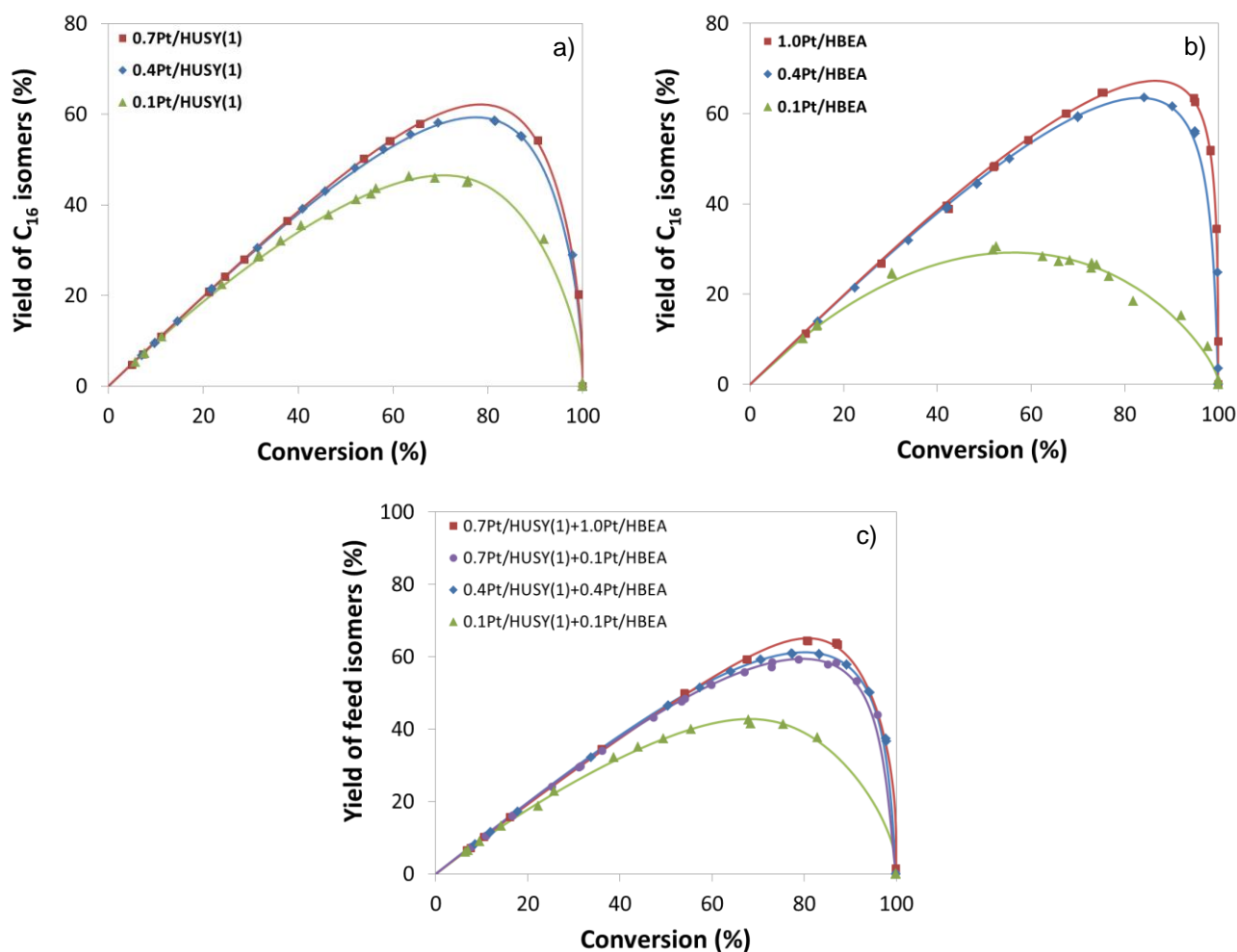
Sample	T @ 50% n-C <sub>16</sub> conversion (K)	TOF <sub>Al</sub> @ 490 K (10 <sup>3</sup> s <sup>-1</sup> )	TOF <sub>Al</sub> @ 513 K (10 <sup>3</sup> s <sup>-1</sup> )	Maximal i-C <sub>16</sub> yield (%)
Pt/HUSY(1)	481	6.5	-	58.9
Pt/HUSY(2)	502	2.7	14.9	62.6
Pt/HMOR	511	-	2.0	44.1
Pt/HZSM-5	520	-	13.9	20.0
Pt/HEU-1	523	-	1.7	42.8
Pt/HNU-10	529	-	1.8	78.3
Pt/HZSM-48	544	-	1.0	57.7
57%Pt/HMOR+Pt/HUSY(2)	504	-	4.0	54.7
78%Pt/HZSM-5+Pt/HUSY(2)	515	-	12.4	36.7
75%Pt/HEU-1+Pt/HUSY(2)	514	-	3.5	51.7
75%Pt/HNU-10+Pt/HUSY(2)	517	-	4.3	65.8
85%Pt/HNU-10+Pt/HUSY(2)	522	-	3.0	68.1
90%Pt/HNU-10+Pt/HUSY(2)	523	-	2.7	70.7
92%Pt/HZSM-48+Pt/HUSY(2)	537	-	2.0	57.7
95%Pt/HZSM-48+Pt/HUSY(2)	541	-	1.6	58.1

### Mixtures of Pt/HUSY(1) and Pt/HBEA catalysts





**Figure B.3:**  $n$ -C<sub>16</sub> conversion as function of reaction temperature for Pt/HUSY a) and Pt/HBEA b) catalysts. Symbols stand for experimental data and lines for model fitting results.



**Figure B.4:** Yield of C<sub>16</sub> isomers as function of conversion for a) Pt/HUSY(1), b) Pt/HBEA and c) Pt/HUSY(1) +Pt/HBEA.

**Table B.2:** Temperature at 50% feed conversion, turnover frequency over protonic sites at 480K and maximum isomer yield for individual catalysts and hybrid catalysts based on 75% Pt/HUSY(1) and 25% Pt/HBEA catalysts mixtures

Sample	T @ 50% n-C <sub>16</sub> conversion (K)	TOF <sub>Al</sub> @ 480 K (10 <sup>3</sup> s <sup>-1</sup> )	Maximal i-C <sub>16</sub> yield (%)
0.1Pt/HUSY(1)	485	1.6	46.5
0.4Pt/HUSY(1)	481	2.1	59.3
0.7Pt/HUSY(1)	484	1.6	62.1
0.1Pt/HBEA	476	3.0	29.2
0.4Pt/HBEA	474	4.0	63.5
1.0Pt/HBEA	471	4.7	67.3
0.1Pt/HUSY(1)+0.1Pt/HBEA	481	2.0	42.9
0.4Pt/HUSY(1)+0.4Pt/HBEA	477	2.9	61.3
0.7Pt/HUSY(1)+0.1Pt/HBEA	478	2.6	59.5
0.7Pt/HUSY(1)+1.0Pt/HBEA	478	2.7	65.1

## Appendix C: Parameters for dual-function kinetic model

### Pt/HUSY(2) and Pt/zeolite catalysts

**Table C.1:** Parameters for  $\text{TOF}_{\text{Al}}$  (Equation 5) and  $Y_{i-\text{C}_{16}}$  (Equation 6) determined by fitting catalytic descriptors results to the dual-function kinetic model.

Zeolites	$\alpha$ ( $10^3 \text{ s}^{-1}$ )	$\gamma$ (%)
Pt/HUSY(1)	-	58.9
Pt/HUSY(2)	14.9	62.6
Pt/HMOR	2.0	44.1
Pt/HZSM-5	13.9	20.0
Pt/HEU-1	1.7	42.8
Pt/HNU-10	1.8	78.3
Pt/HZSM-48	1.0	57.7

### Pt/HUSY(1) and Pt/HBEA catalysts

**Table C.2:** Parameters for  $\text{TOF}_{\text{Al}}$  (Equation 3) and  $Y_{i-\text{C}_{16}}$  (Equation 4) determined by fitting catalytic descriptors results to the dual-function kinetic model.

Sample	$\alpha$ ( $10^3 \text{ s}^{-1}$ )	$\beta$ ( $10^3$ )	$\gamma$ (%)	$\epsilon$ ( $10^3$ )
Pt/HUSY(1)	2.0	0.69	65.6	1.4
Pt/HBEA	5.2	2.0	84.0	4.5