

Supporting Information

for

High-performing Ir- and Pt-containing catalysts based on mesoporous beta zeolite for the selective ring opening of decalin

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Figure S1. Decalin conversion and yield to the overall C₁₀ and C₉ product fractions as a function of time-on-stream (TOS) for Ir(Pt)/Cs-beta catalysts at the reaction temperatures of 240 and 260 °C. Conditions: P = 3.5 MPa, WHSV = 0.44 h⁻¹, H₂/decalin = 100 mol/mol.

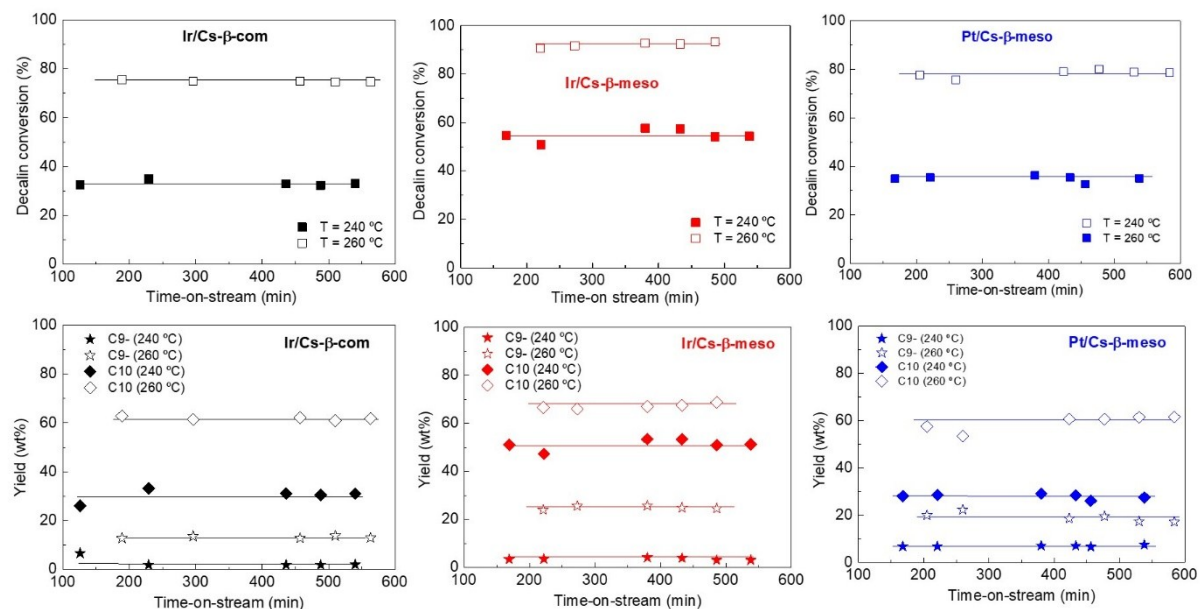
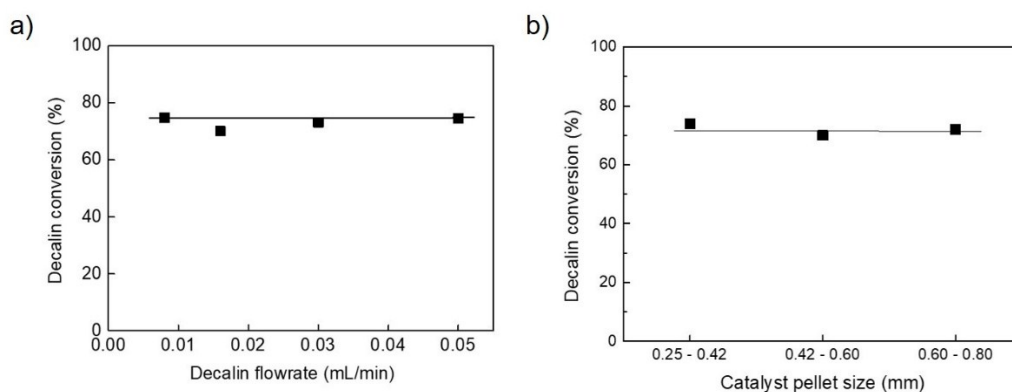


Figure S2. Preliminary catalytic tests with the Ir/Cs- β -com catalyst showing the absence of external (a) and internal (b) mass transfer limitations at the studied reaction conditions.



a) The influence of external mass transfer was assessed by simultaneously varying the decalin flowrate (0.005 – 0.025 mL/min) and the catalyst mass loaded in the reactor (0.6 – 3.0 g) so as to maintain a constant weight hourly space velocity (WHSV) of 0.44 h⁻¹ at the reaction temperature of 260 °C (P = 3.5 MPa, H₂/decalin = 100 mol/mol).

b) For evaluating the influence of internal mass transfer, catalytic tests were carried out varying the catalyst pellet size range (0.25 – 0.42 mm, 0.42 – 0.6 mm, 0.6 – 0.8 mm) using a decalin flowrate of 0.008 mL/min and a mass of catalyst of 1.0 g, corresponding to WHSV of 0.44 h⁻¹ (P = 3.5 MPa, H₂/decalin = 100 mol/mol).

Based on these preliminary experiments, we selected a decalin flow rate of 0.008 mL/min and a mass of catalyst of 1.0 g (WHSV = 0.44 h⁻¹) with a pellet size of 0.25 – 0.42 mm for performing the decalin ring opening experiments to ensure the absence of diffusion restrictions and, thus, to compare the catalytic performance of Ir(Pt)/Cs-beta catalysts under kinetic regime.

Figure S3. Typical GCxGC chromatogram obtained in the (hydro)conversion of decalin on the bifunctional Ir(Pt)/Cs-beta catalysts, identifying the different hydrocarbon families: light products (C_9 -), *cis*- and *trans*-decalin (*cis*- and *trans*-D), decalin isomers (isoD), C_{10} -alkylcyclohexanes (ROP), and open-chain decanes (OCD).

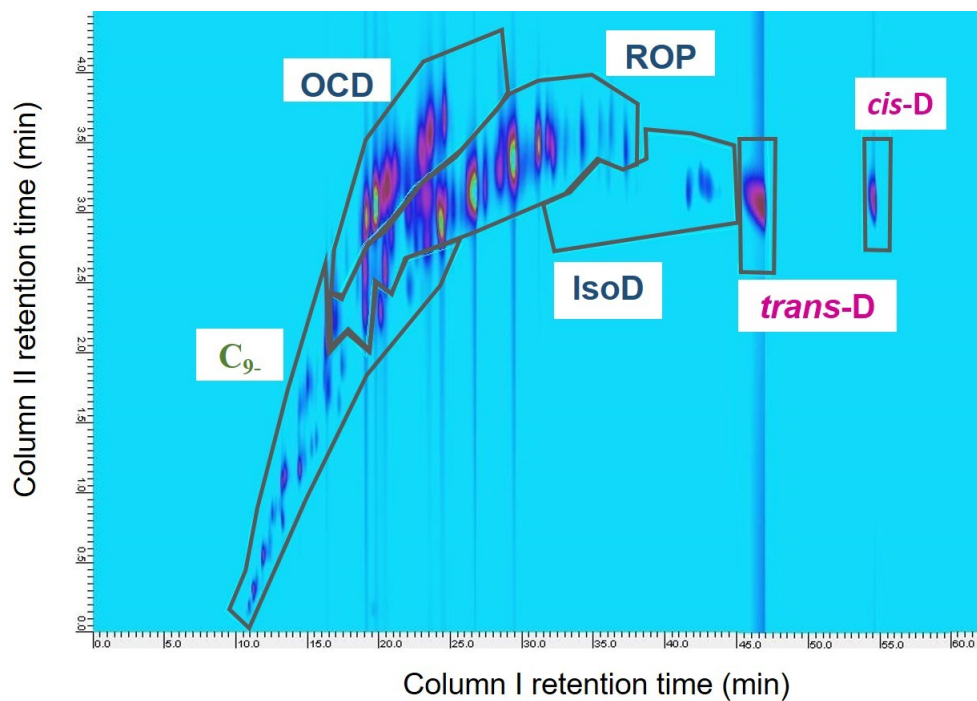
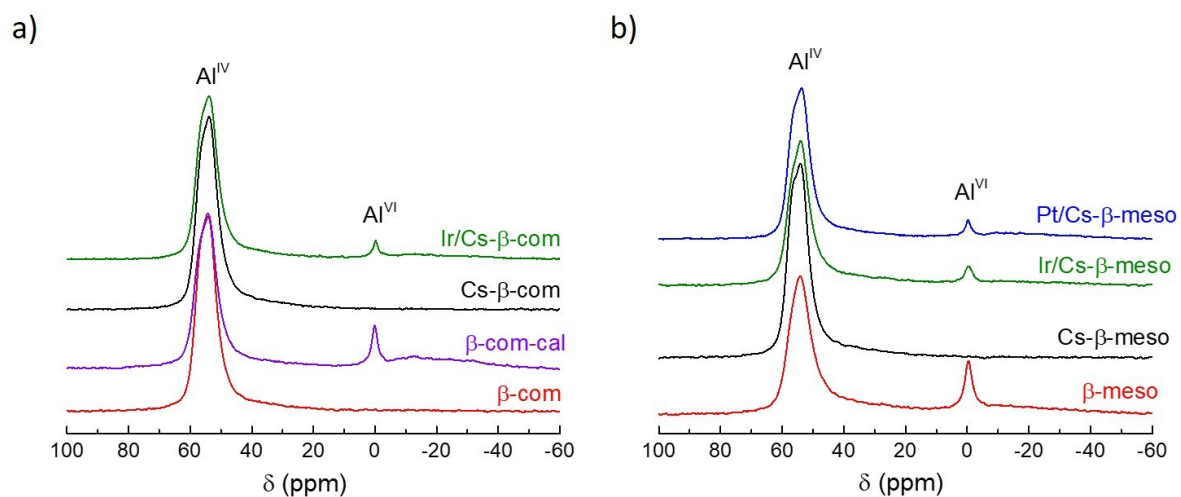


Figure S4. ^{27}Al MAS NMR spectra of fully hydrated commercial (a) and mesoporous beta (b) zeolites at different catalyst preparation stages: starting zeolites, after $\text{Na}^+ + \text{Cs}^+$ ionic exchange, and after metal incorporation and subsequent calcination. The spectra are normalized to sample weight.



As seen in panel a, while the original commercial NH_4^+ -beta sample (β -com) was virtually free of extraframework Al (EFAL) species ($\delta \sim 0$ ppm), some EFAL formed upon calcination of β -com applied prior to ionic exchange with alkali ($\text{Na}^+ + \text{Cs}^+$) cations (sample β -com-cal). On the other hand, the alkaline treatment of EFAL-free β -com (NH_4^+ -form) lead to the formation of EFAL species (β -meso, panel b).

Figure S5. IR spectra in the –OH stretching vibration region for bare β -com and β -meso zeolites.

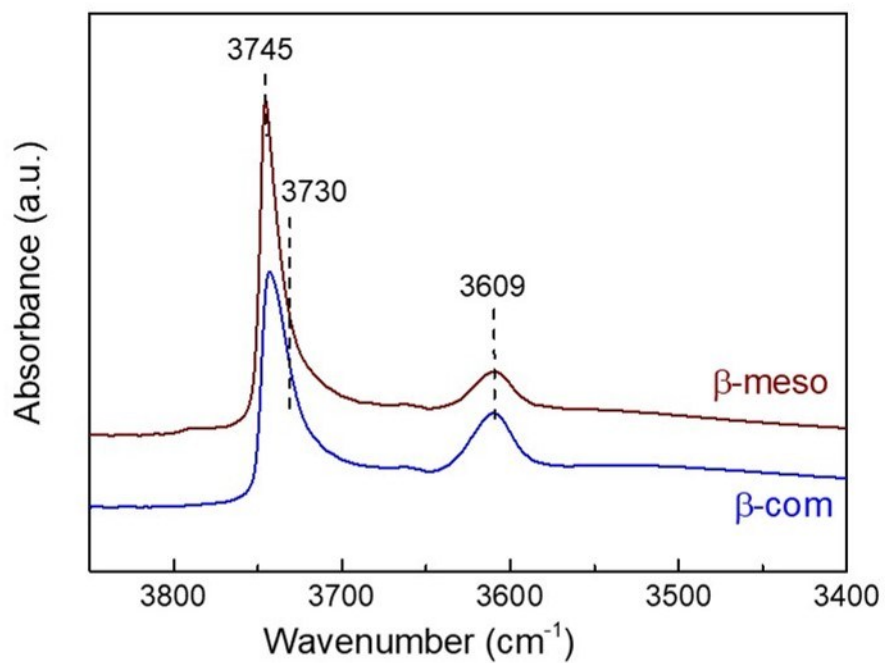
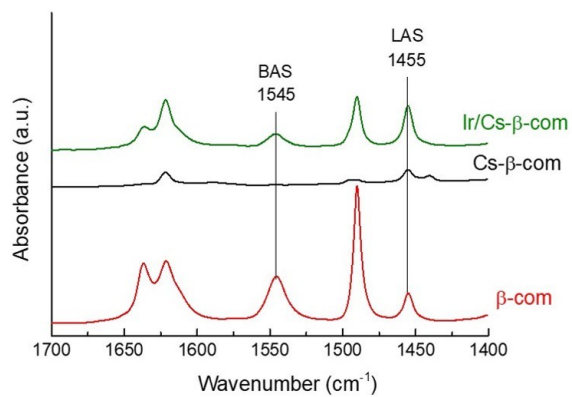


Figure S6. FTIR spectra in the pyridine vibration region at a pyridine desorption temperature of 250 °C for the series of zeolites and catalysts based on the commercial (a) and the mesoporous (b) beta zeolites.

a)



b)

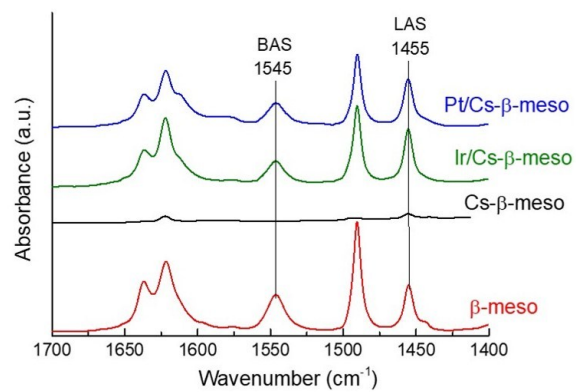
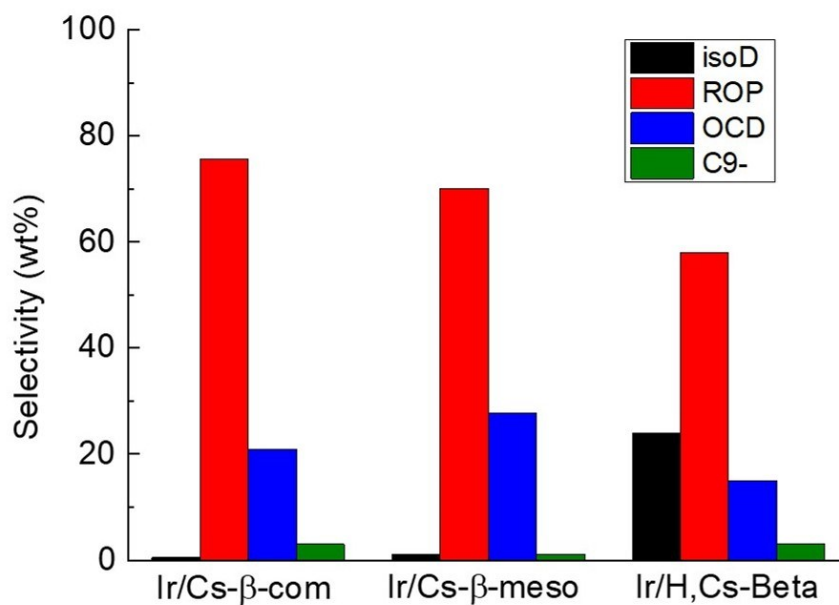


Figure S7. Product selectivities at low decalin conversion (20 – 25%) for previously reported Ir/Cs-Beta HIPEROC¹ and for the Ir/Cs- β catalysts studied in this work at equivalent Ir loading (3.0 – 3.5 wt%).



¹ Data corresponding to catalyst 3.4Ir/H,Cs-Beta in Figure 3 of the work by Santi et al. in Applied Catalysis A 455 (2013) 46-57.

Table S1. Comparison of the maximum yields of open chain decanes (OCD) and combined yields of OCD and ring opening products (ROP+OCD) achieved in the conversion of decalin over the mesoporous Ir/Cs- β -meso catalyst in this work and over previously reported HIPEROX systems.

Catalyst	T (°C)	X _{Dec} (%)	Y _{OCD,max} (wt%)	Y _{OCD,max+ROP} (wt%)	Reference
Ir/Cs- β -meso	255	89	32	73	This work
Pt/Na,H-Y	361	96	39	54	[1]
3.0Ir/Na,H-Beta	246	90	34	59	[2]
3.4Ir/H,Cs-Beta	262	94	44	59	[2]

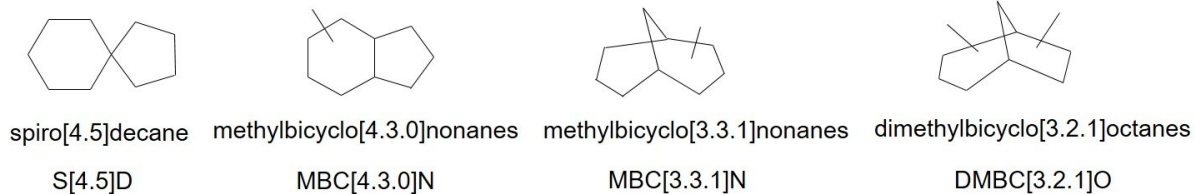
References

[1] S. Rabl, D. Santi, A. Haas, M. Ferrari, V. Calemma, G. Bellussi, J. Weitkamp, *Microp. Mesop. Mater.* 146 (2011) 190-200.

[2] D. Santi, T. Holl, V. Calemma, J. Weitkamp, *Appl. Catal. A* 455 (2013) 46-57.

Figure S8. a) Main isoD hydrocarbons identified by GCxGC-MSD in the conversion of decalin over the Pt/Cs- β -meso catalyst, and b) evolution of their yields with decalin conversion. The abbreviation used to denote each decalin isomer is given below the full name in a).

a)



b)

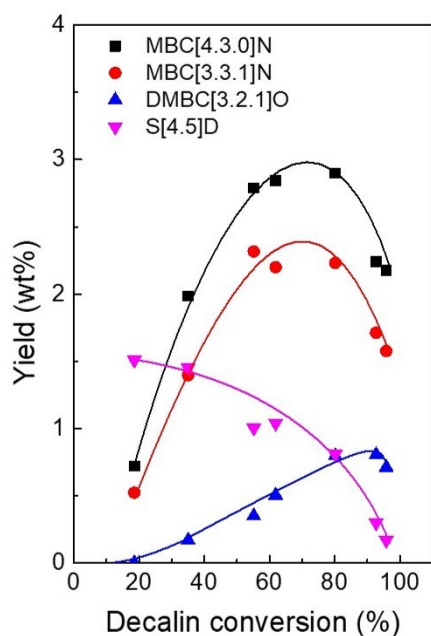
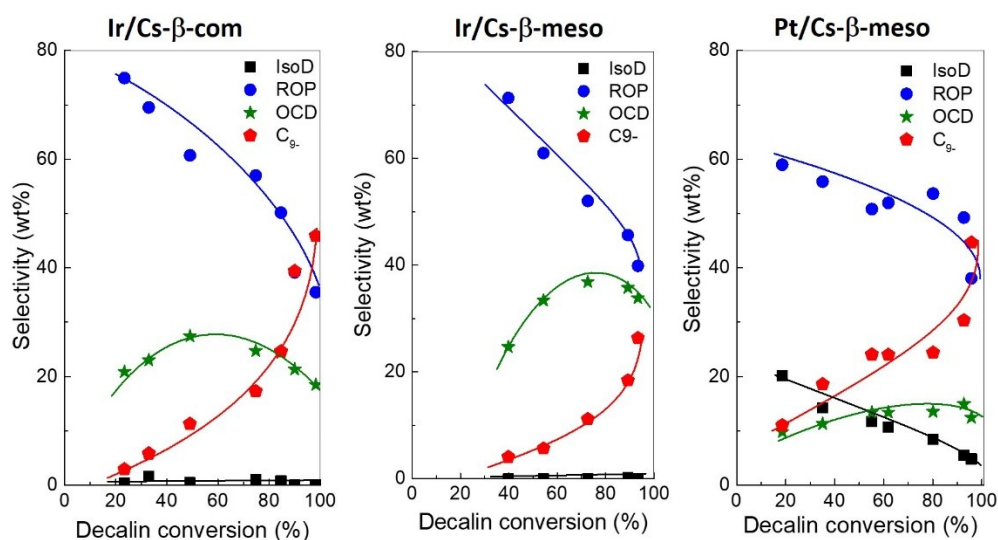


Figure S9. a) Selectivity to the different product fractions as a function of decalin conversion for the Ir(Pt)/Cs- β catalysts; b) General reaction schemes for the conversion of decalin on the Ir- and Pt-based catalysts studied in this work. Reaction conditions: T = 220 – 275 °C, P = 3.5 MPa, WHSV = 0.44 h⁻¹, H₂/decalin = 100 mol/mol.

a)



b)

