Extended Supplementary Information for:

Hierarchically porous BEA stannosilicates as unique catalysts for bulky ketone conversion and continuous operation

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Figure S1a. TEM image of dealuminated zeolite beta. The presence of micropores and the absence of major mesopores following dealumination is clear, and confirms the porosimetry analysis.



Figure S1c. TEM image of 2Sn-h*beta.



Figure S1b. Literature image of microporous zeolite beta. Image taken from J.C. Groen et al. / Microporous and Mesoporous Materials 114 (2008) 93–102.



Figure S1d. Literature image of desilicated ZSM-5. Image taken from J.C. Groen et al. / Microporous and Mesoporous Materials 69 (2004) 29-34.



Figure S1e. Initial TEM image of dealuminated zeolite beta



Figure S1f. TEM image of dealuminated zeolite beta after some time under the beam.

Figure S1. A selection of preliminary TEM measurements.



Figure S2. Porosimetry data for 2Sn-MCM-41.



Figure S3. SEM images of A) parent zeolite β , B) 2Sn- β , C) 2Sn-h* β and D) 2Sn-MCM-41 obtained at 15kV and EDX observation conditions.



Figure S4. In situ CD_3CN -DRFITS spectra of 2Sn-MCM-41, following (dashed) 10 minutes treatment with CD_3CN at room temperature. Various desorption temperatures (50 (red), 100 (blue), 150 (purple) and 200 °C (green)) are also displayed.



Figure S5. Geometry optimised structures of C_6 - C_8 ketones (B3LYP/6-31Gd), and relative values of diameter calculated by a combination of theoretical and experimental values. The estimated effective diameter was calculated by taking the distance between the centre of two carbon atoms along the largest direction of the carbon ring (r, indicated on the molecules), and adding the two atomic radii of the same carbon atoms, leads to the following calculated sizes: **4.4, 5.0 and 6.1 Å.** Although this underestimates the actual kinetic diameter, it provides a useful "relative value" that can be compared to known literature values.

Entry	Known	Calculated	Diameter,	Relative	Estimated	Relative	Approximate
	kinetic	molecular	based on	diameter	effective	effective	kinetic
	diameter	volume (Å ³	molecular	based on	diameter	diameter	diameter
	(Å)	molecule ⁻	volume	molecular	from	from	(relative to
		¹) [1]	[1]	volume	calculation	calculation	cyclhexanone)
				[1]	(B3LYP) (Å)	(B3LYP)	
<i>C</i> ₆ =0	6.0*	101.06	5.8	1	4.4	1	6.0
<i>C</i> ₈ =0	-	133.97	6.3	1.1	5.0	1.1	6.6
<i>C</i> ₁₂ = <i>O</i>	-	-	-	-	6.1	1.4	8.4

[1] C. E. Webster, R. S. Drago, M. C. Zerner, J. Am. Chem. Soc. 1998, **120**, 5509-5516. *Stated for cyclohexane



Figure S6. XRD pattern of $2Sn-\beta$ dispersed in SiC after 200 h on stream, displaying retention of crystalline structure during continuous operation.

Table S1. EDX analysis for element quantification

	O (Wt. %)	Si (Wt. %)	Al (Wt. %)	Sn (Wt. %)
Parent zeolite β	54.8	43.4	1.8	0
deSi <i>,</i> Al-β	65.3	34.7	0	0
2Sn-h*β	54.1	43.8	0	2.1
2Sn-β	55.5	42.5	0	2.0

EDX analysis conditions: Uncoated samples using a Silicon detector and accelerating voltage of 25 kV

Synthesis 2Sn-MCM-41:

An aqueous solution of hexadecyltrimethyl-ammonium bromide (C_{16} TMABr) (Sigma-Aldrich, 99%), tetramethylammonium hydroxide solution (25%, Sigma-Aldrich) and tin (IV) chloride pentahydrate (Sigma-Aldrich, 98%) were mixed under continuous stirring. After homogenisation, fumed silica (Sigma-Aldrich, 99%) was slowly added and the gel was further homogenised for 2 h. The final molar composition was $1SiO_2$: $0.08C_{16}$ TABr: $0.08C_{16}$ TAOH: 0.26TMAOH: $0.02SnCl_4$: $24.3H_2O$. The homogeneous gel was transferred to a stainless steel autoclave (125 mL capacity) and crystallized at 135 °C for 24 h. The organic template was removed by heating at 540°C for 1 h in N₂ flow, followed by 6 h in air.

Plug flow reactor conditions:

Continuous reactions were performed in a plug flow, stainless steel, tubular reactor connected to an HPLC pump in order to regulate the reactant flow. The catalyst was mixed with a diluent material (SiC) to minimise backmixing and excessive pressure drop, and placed between two plugs of quartz wool. The diluted sample was densely packed into a $\frac{1}{4}$ " stainless steel tube (4.1 mm internal diameter), and a frit of 0.5 µm was placed at the end of the catalytic bed in order to avoid any loss of materials. The reactor was subsequently immersed in a thermostatted oil bath at the desired reaction temperature. Pressure in the system was controlled by means of a backpressure regulator, and the pressure drop was determined by comparison of the HPLC pump pressure to the outlet pressure measured by a pressure gauge. An overpressure of 5 bar was typically employed. Aliquots of the reaction solution were taken periodically from a sampling valve placed after the reactor column. Catalyst regeneration was performed heating the whole reactor in a combustion furnace (Carbolite MTF12/38/400) to 550 °C (10 °C min⁻¹) in air (3 h).