

Supplementary Information

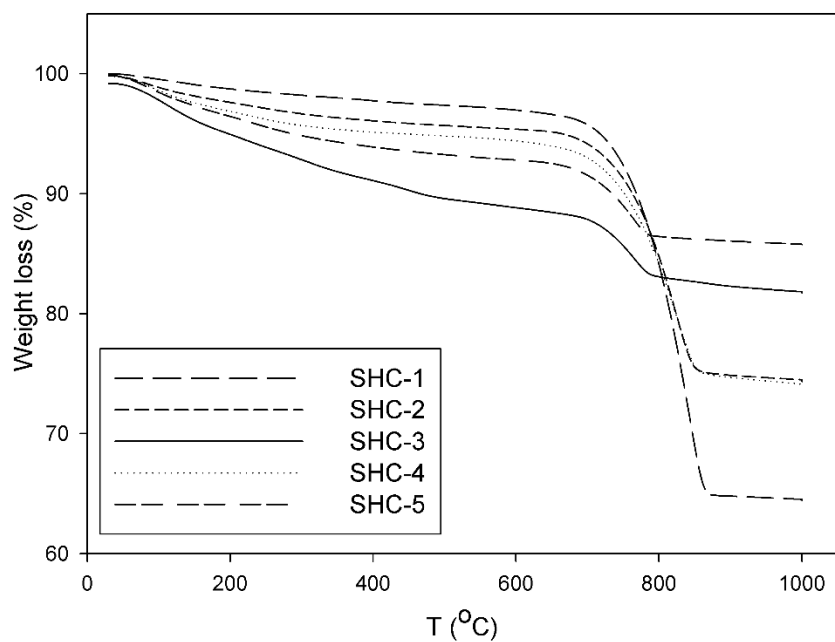
Structured hydroxyapatite composites as efficient solid base catalysts for condensation reactions

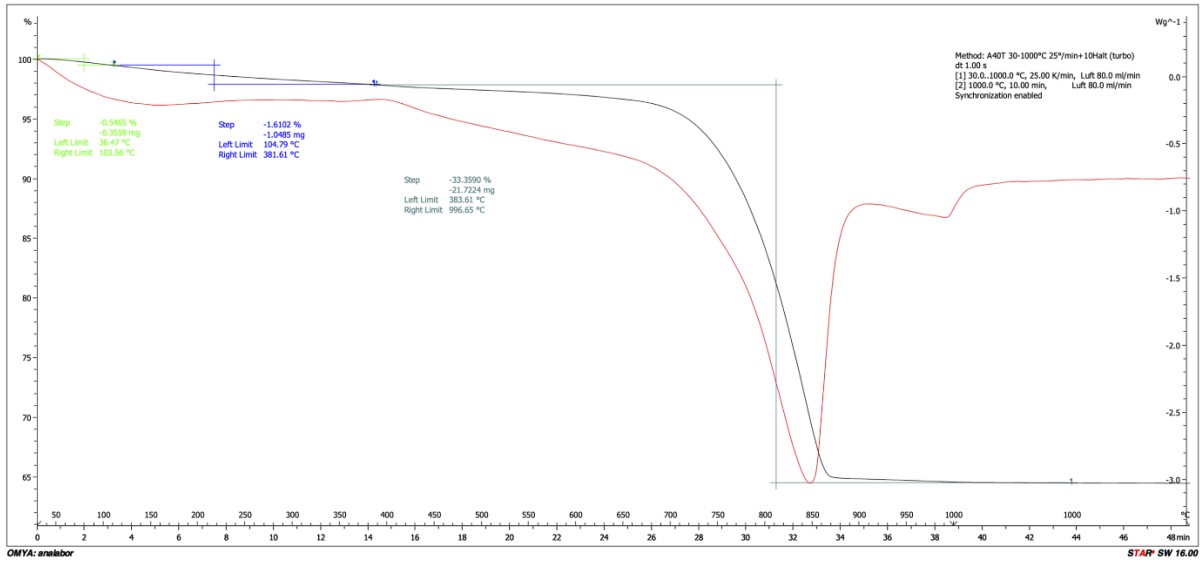
Tharun Jose, Jamal Ftouni and Pieter C. A. Bruijninx*

Table S1. Phase composition based on quantitative Rietveld analysis of the SHC samples.

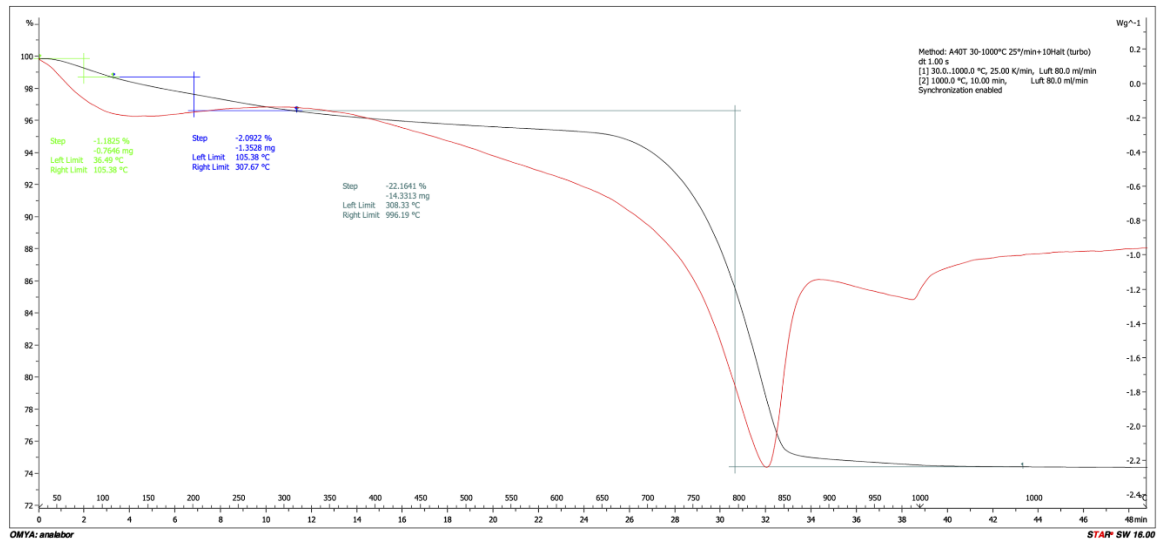
Samples	Calcite (CaCO ₃)	Hydroxyapatite (Ca ₅ (PO ₄) ₃ (OH))	Octa-Ca Phos. (Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O)	Total
SHC-1	79	21	-	100
SHC-2	50	50	-	100
SHC-3	15	85	-	100
SHC-4	14	86	-	100
SHC-5	11	79	10	100

Data were normalized to 100% crystalline material; Octa-Ca Phos. = Octacalcium phosphate.

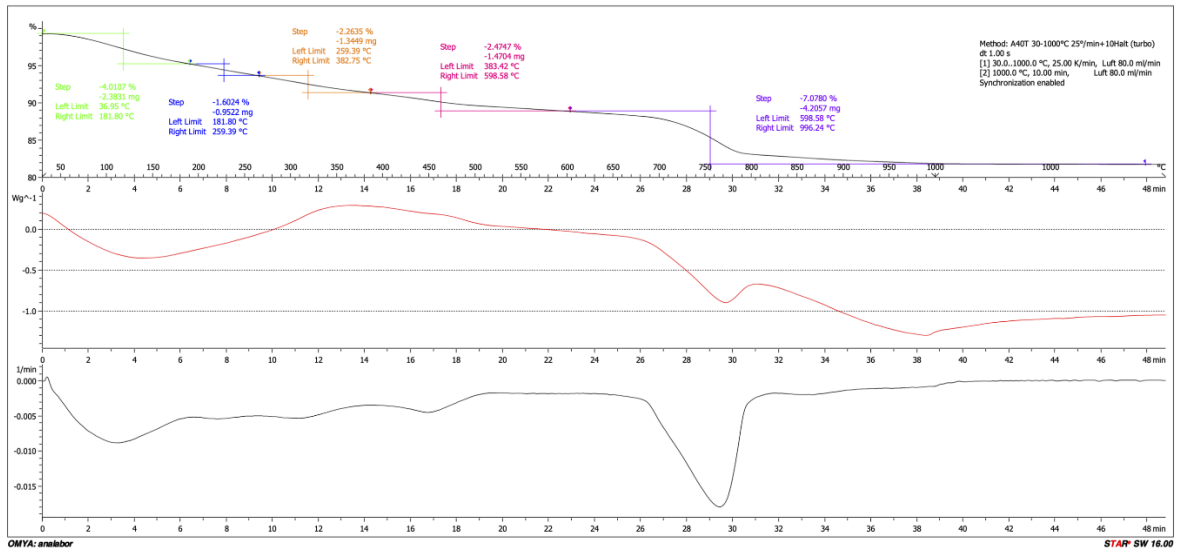




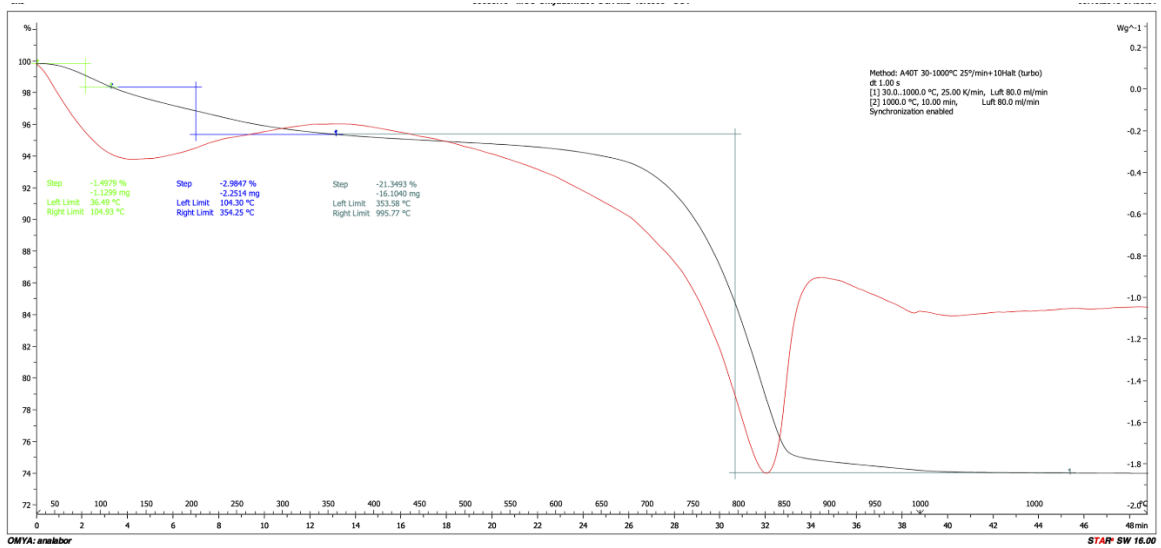
SHC-1



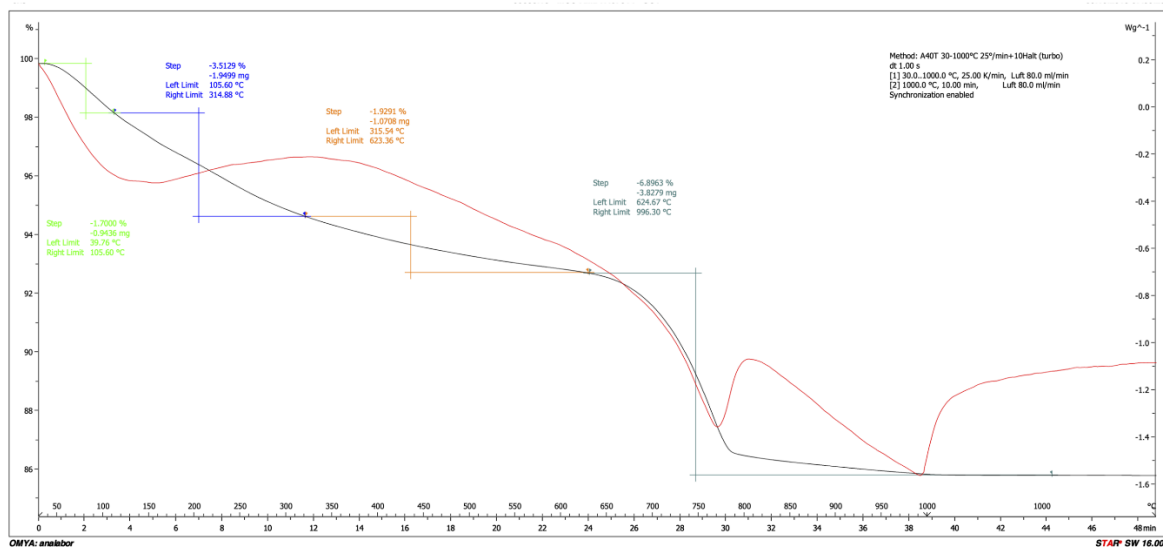
SHC-2



SHC-3



SHC-4



SHC-5

Figure S1. Thermal analysis- TGA/DSC curves of the SHC samples.

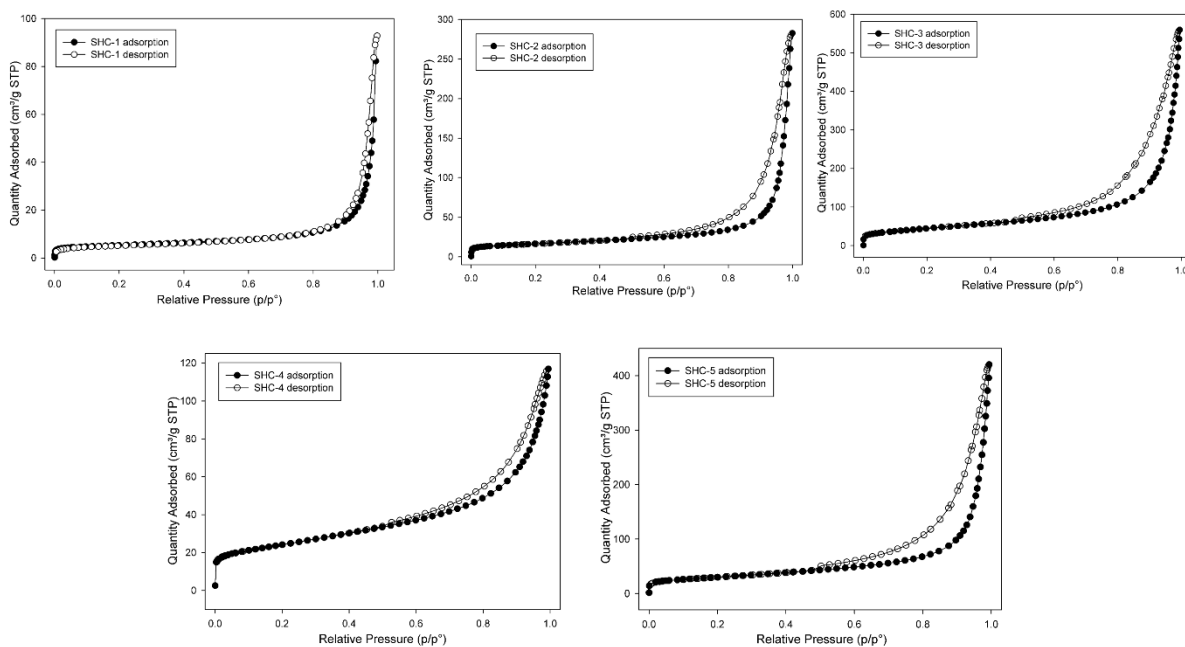


Figure S2. The nitrogen adsorption/desorption isotherm plots for the SHC catalysts.

Table S2. Literature survey of various catalysts employed for the self-aldol condensation reactions.

Entry	Catalyst	Cat. amount (g)	Cat. Loading (mol%)	Aldehyde	Temp. (°C)	Time (h)	Conversion (%)	Reference
1	SFIL		10	Butyraldehyde	120	6	89.4	1
2	MOS2	0.1	-	Butyraldehyde	100	10	83	2
3	Amino functionalized chitosan	0.05	-	Butyraldehyde	100	8	96	3
4	Nb ₂ O ₅	2	-	Butyraldehyde	200	5	48.5	4
5	SiO ₂ -Al ₂ O ₃	2	-	Butyraldehyde	200	5	29.3	4
6	MgO-ZrO ₂		10	Cyclopentanone	130	6	84	5
7	CaC ₂	4	36	Acetone	130	10	>90	6
8	Ce-MgAl-Hydrotalcite	0.5	-	Acetone	0	6	20	7

SFIL = [HSO₃-b-N(ET)₃]p-TSA; MOS2 = MgCl₂.6H₂O + APTMS; Solvent-free conditions; Cat. = Catalyst; Temp. = Temperature.

Table S3. Self-aldol condensation reaction of butyraldehyde based upon catalyst weight percentage loading.

Entry	Catalyst	Time (h)					
		2		6		22	
		X (%)	Y (%)	X (%)	Y (%)	X (%)	Y (%)
1	SHC-3	67	67	91	89	100	98
2	HAP-H	10	10	53	53	70	68

Reaction conditions: Temperature = 130 °C; Catalyst loading = 17 wt.%; X = conversion, Y = yield, Results from NMR; IS = Mesitylene; HAP = Hydroxyapatite.

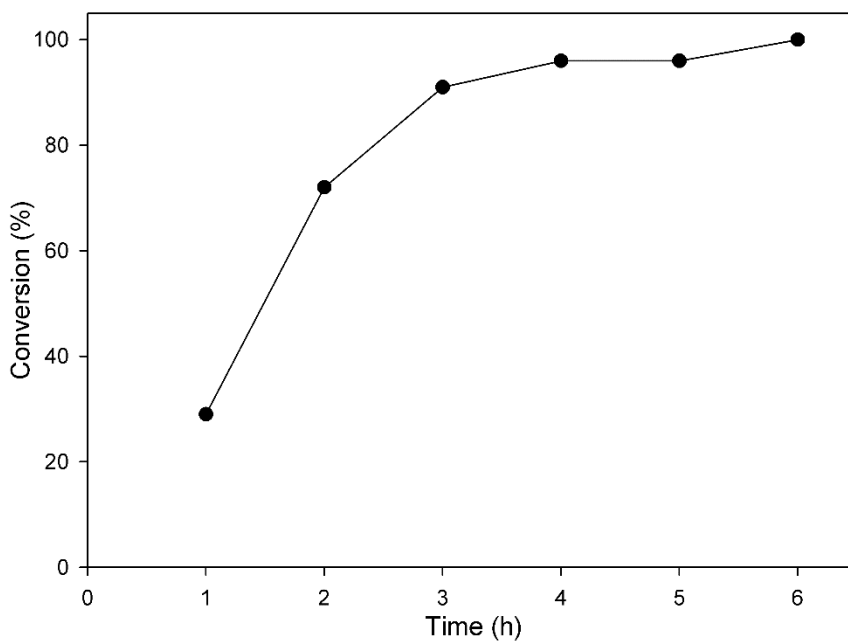


Figure S3. Dependence of butyraldehyde conversion on reaction time.

Reaction conditions: Catalyst = SHC-3; Catalyst loading = 3 mol%; Temperature = 130 °C; Selectivity at 1 h and 2 h \geq 99%, from 3 h to 6 h = 97%; Results from NMR; IS = Mesitylene.

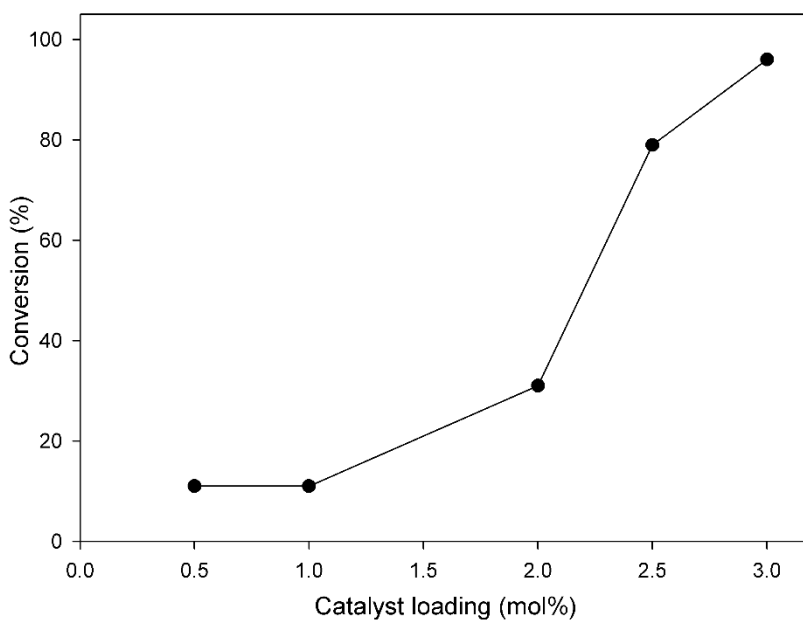


Figure S4. Dependence of Butyraldehyde conversion on catalyst loading.

Reaction conditions: Catalyst = SHC-3; Temperature = 130 °C; Time = 4 h; Selectivity from 0.5 to 2 mol% \geq 99%, 2.5 mol% = 98%, 3 mol% = 97%; Results from NMR; IS = Mesitylene.

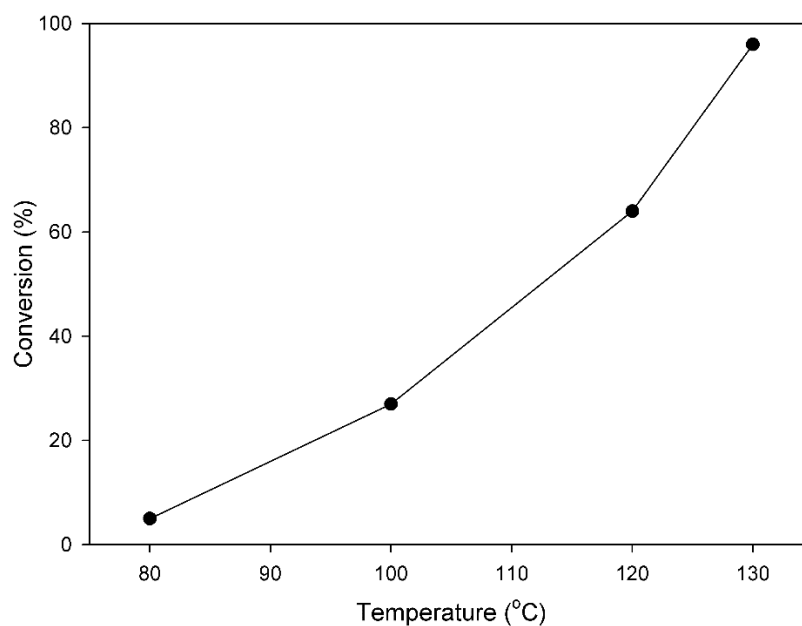


Figure S5. Dependence of Butyraldehyde conversion on reaction temperature.

Reaction conditions: Catalyst = SHC-3; Catalyst loading = 3 mol%; Reaction time = 4 h; Selectivity from 80 to 100 °C \geq 99%, for 110 and 120 °C = 98%, 130 °C = 97%; Results from NMR, IS = Mesitylene.

Table S4. Number of acidic and basic sites as determined by NH_3 and CO_2 -TPD, respectively.

Entry	Catalyst	CO_2 -TPD			NH_3 -TPD		
		Number of basic sites (mmol/g)			Number of acidic sites (mmol/g)		
		Weak	Medium	Total	Weak	Medium	Total
1	SHC-1	0.05	-	0.05	-	0.03	0.03
2	SHC-2	0.01	0.07	0.08	-	0.09	0.09
3	SHC-3	0.05	0.28	0.33	-	0.19	0.19
4	SHC-4	0.08	0.07	0.15	-	0.13	0.13
5	SHC-5	0.03	0.05	0.08	-	0.12	0.12
6	HAP-L	0.06	-	0.06	-	0.02	0.02
7	HAP-H	0.02	0.11	0.13	-	0.11	0.11

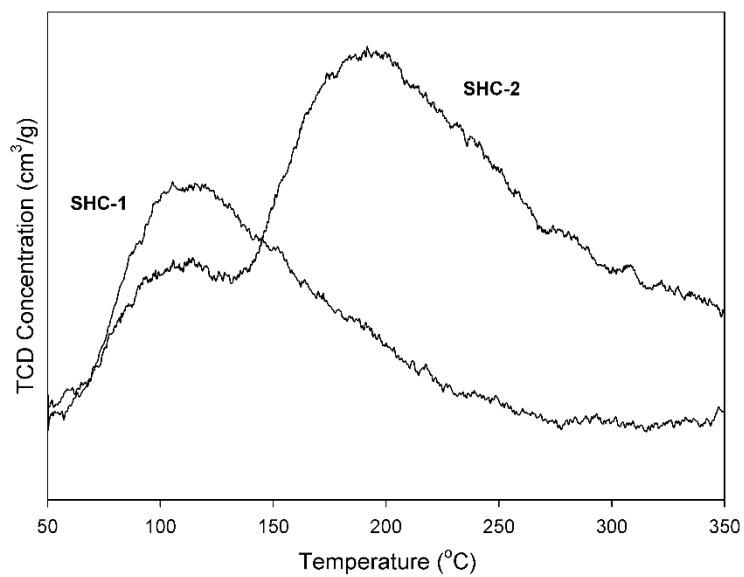


Figure S6. CO₂-TPD curves for the SHC-1 and SHC-2 catalysts.

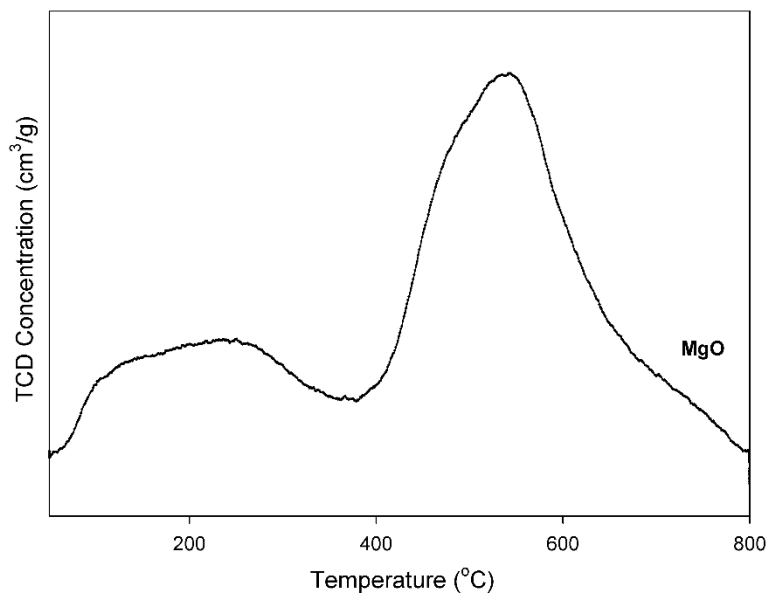


Figure S7. CO₂-TPD curves for MgO. Total number of basic sites: 0.97 mmol/g.

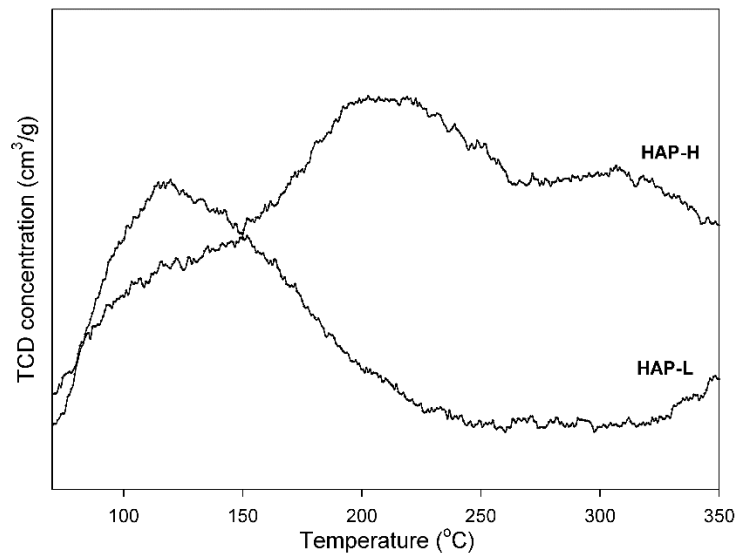


Figure S8. CO₂-TPD curves for HAP-H and HAP-L.

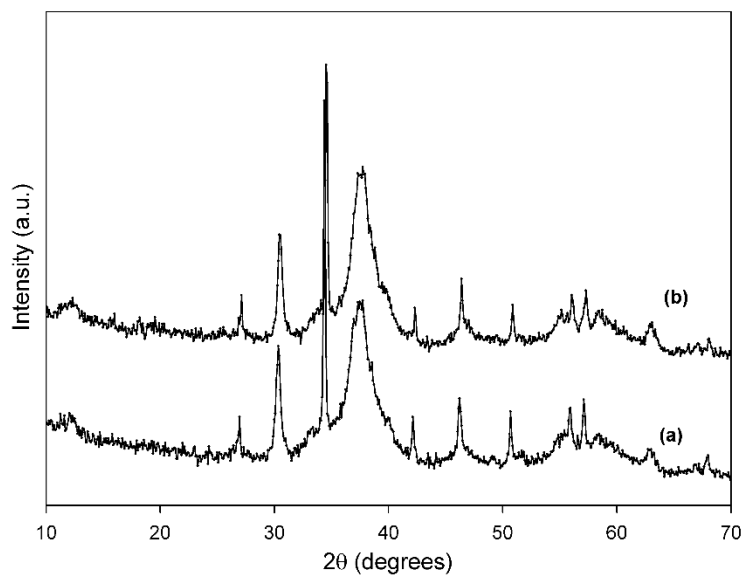


Figure S9. XRD structures for the fresh and recycled SHC-3 catalyst (entry 1, Table 5). (a) fresh, (b) after 1st recycle.

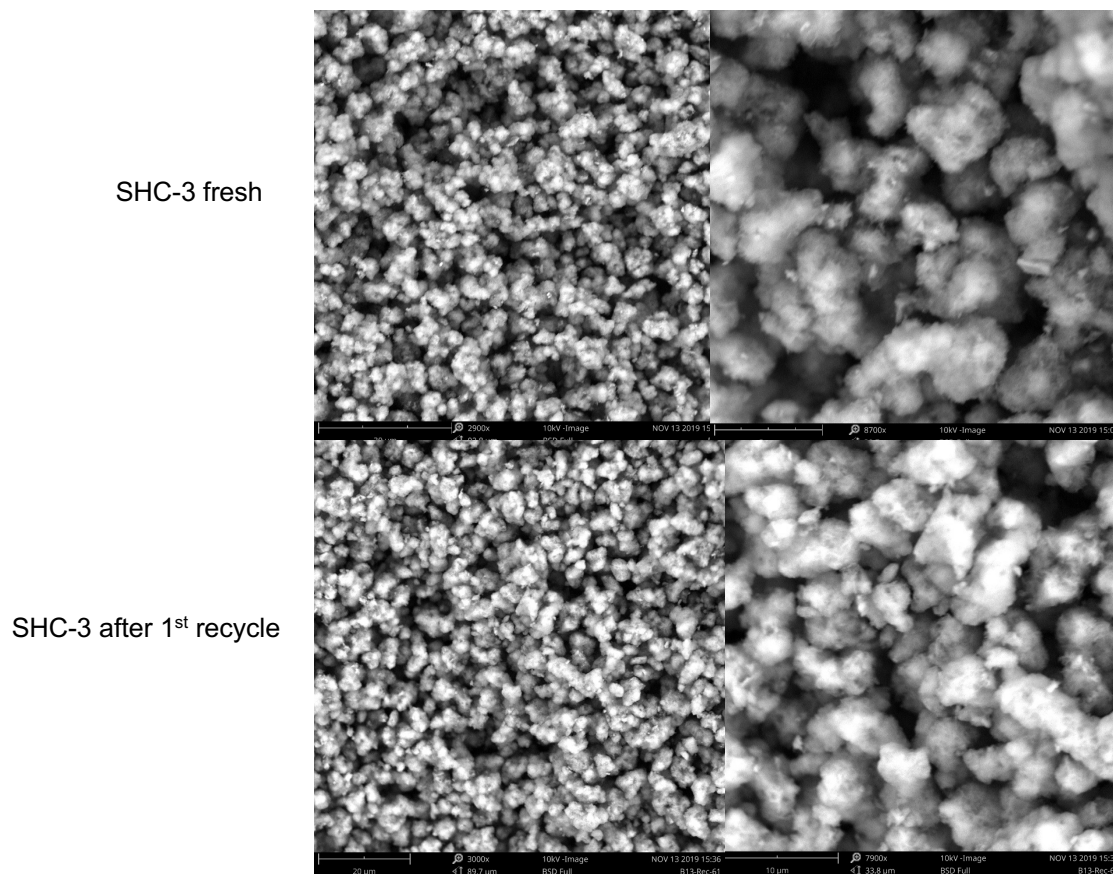


Figure S10. SEM images for the fresh and recycled SHC-3 catalyst (entry 1, Table 5).

Table S5. ICP and elemental analysis for SHC-3 catalyst (entry1, Table 5).

Entry	Run	ICP-OES			EA
		Ca (wt%)	P (wt%)	Ca/P ratio	C (wt%)
1	1 (Fresh)	40.67	6.34	4.95	3.8
2	after 1 st recycle	38.84	5.75	5.10	6.9
3	Filtrate	-	-	-	n.d.

Filtrate = from entry1, table 5 after 1st recycle; n.d. = not determined.

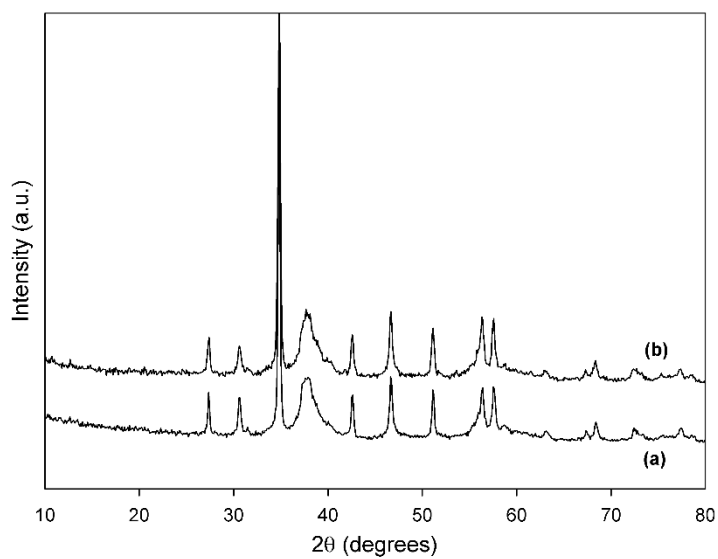


Figure S11. XRD structures for the fresh and recycled SHC-4 catalysts (entry 3, Table 5). (a) = fresh, (b) = after 4th recycle.

Table S6. BET analysis and CO₂-TPD for the fresh and recycled catalysts (entry 1 and 3, Table 5).

Entries from Table 5	Run	SHC	BET (m ² /g)	CO ₂ -TPD Total number of basic sites (mmol/g)
1	1 (Fresh)		160.3	0.33
	after 4 th recycle	SHC-3	125.3	0.05
3	1 (Fresh)		85.5	0.15
	after 4 th recycle	SHC-4	67.2	0.08

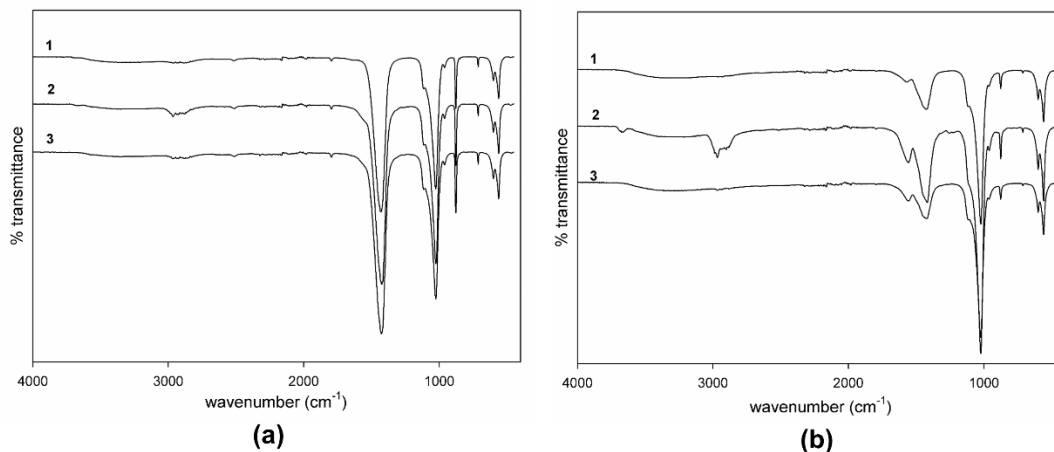


Figure S12. FT-IR for the fresh and recycled SHC catalysts: (a) SHC-4 and (b) SHC-3. (1) Fresh, (2) after 1st recycle and (3) after 4th recycle.

E1. Adsorbed Ammonia and Adsorbed Carbon Dioxide Temperature Programmed Desorption (NH₃-TPD and CO₂-TPD)

The measurements were performed using a Micromeritics ASAP2920 apparatus. 0.1 g of sample was dried in situ under an He flow with a temperature ramp of 5 °C min⁻¹ up to 400 °C.

For the NH₃-TPD measurements, the sample was cooled to 100 °C. At this point, 20 pulses of 5 cm³ 10 vol.-% NH₃ in He were dosed over the sample (corresponding to an NH₃ flow of 25.3 cm³ min⁻¹). The sample was then heated to 600 °C with a ramp of 5 °C min⁻¹ to induce desorption of NH₃. The amount of NH₃ desorbed over time was determined using a thermal conductivity detector (TCD). The TCD concentration was plotted over time for the quantitative evaluation and over temperature to determine the temperature position of the desorption peaks. In both cases, a peak deconvolution was performed. To obtain the total amount of desorbed NH₃, a baseline subtraction and full integration of the desorption feature has been performed. Peak deconvolution was performed using the software Fityk.

After obtaining the area under the curve (AUC, A) (from Fityk), the AUC is converted into a quantifiable amount of NH₃ (n_{NH₃} in mmol/g) using the below formulae:

$$A_r = A / 100 \%$$

$$V_{\text{NH}_3, \text{abs}} = A_r \cdot V$$

$$V_{\text{NH}_3} = V_{\text{NH}_3, \text{abs}} / m_{\text{sample}}$$

$$m_{\text{NH}_3} = V_{\text{NH}_3} \cdot \rho_{\text{NH}_3}$$

$$n_{\text{NH}_3} = m_{\text{NH}_3} / M_{\text{NH}_3}$$

$$\rho_{\text{NH}_3} = 0.76 \text{ kg/m}^3, M_{\text{NH}_3} = 17 \text{ g/mol}$$

A = obtained Area (% • min), A_r = Area (min), V = Flow 25.2 (cm³ / min)

V_{NH₃,abs} = absolute amount of desorbed NH₃ (cm³)

V_{NH₃} = amount of desorbed NH₃ per g of sample (cm³ / g)

For the CO₂-TPD measurements, the sample was cooled to 50 °C and a procedure similar to the one described for NH₃-TPD was employed. The number of basic sites was determined according to the calculation above, using the values $\rho_{\text{CO}_2} = 1.98 \text{ kg/m}^3$ and $M_{\text{CO}_2} = 44.01 \text{ g/mol}$. For calculating the number of acidic or basic sites, it was assumed that only one molecule of NH₃ or CO₂ can adsorb on a single site.

References

1. X. Zhang, H. An, H. Zhang, X. Zhao, Y. Wang, *Ind. Eng. Chem. Res.*, 2014, 53, 16707.
2. H. A. Patel, S. K. Sharma, R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2008, 286, 31.
3. T. Jose, N. Sudheesh, R. S. Shukla, *J. Mol. Catal. A: Chem.*, 2010, 333, 158.
4. D. Sun, S. Moriya, Y. Yamada, S. Sato, *Appl. Catal. A: Gen.*, 2016, 524, 8.
5. D. Liang, G. Li, Y. Liu, J. Wu, X. Zhang, *Catal. Commun.*, 2016, 81, 33.
6. X. Xu, H. Meng, Y. Lub, C. Li, *RSC Adv.*, 2018, 8, 30610.
7. Z. Wang, P. Fongarland, G. Lu, N. Essayem, *J. Catal.*, 2014, 318, 108.