# Electronic Supporting Information

# Facile route to conformal hydrotalcite coatings over complex architectures: a hierarchically ordered nanoporous base catalyst for FAME production

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## Catalyst synthesis

### Synthesis of macroporous-mesoporous SBA-15 (MM-SBA-15)

An hierarchical macroporous-meosporous SBA-15 silica was prepared following the method of Dhainaut et al.[60] Polystyrene beads (45 g) synthesised using the emulsion polymerisation approach of Vaudreuil and co-workers[61] were added to an acidified, aqueous solution of Pluronic® P123 triblock co-polymer surfactant (10 g of P123 dissolved in 75 cm$^3$ of water and 290 cm$^3$ of 2 M HCl solution) and stirred for 1 h prior to the addition of tetramethoxysilane (15 cm$^3$). The resulting gel was hydrothermally aged for 24 h at 100 °C without agitation. The solid obtained was filtered, washed with water (1000 cm$^3$) and dried at room temperature before calcination at 550 °C for 6 h in air (ramp rate 0.5 °C.min$^{-1}$).

### Alumina grafting onto MM-SBA-15 (Al-MM-SBA-15)

The Al-MM-SBA-15 hierarchical framework was adapting from the method of Landau and co-workers developed for MCM-41.[62] Aluminium-tri-sec-butoxide (14.5 g) was dissolved in anhydrous toluene (100 cm$^3$) at 85 °C with stirring. Triethylamine (2.1 cm$^3$) was added to this solution, followed by dried MM-SBA-15 (1 g). After 6 h stirring at 85 °C the solution was filtered under vacuum (~0.1 bar) to recover the solid, which was washed three times in toluene (100 cm$^3$). The alumina surface was then hydrolysed in ethanol (318 cm$^3$) containing water (1.6 cm$^3$) for 24 h at 25 °C with stirring, and the resulting solid product recovered by vacuum filtration and washed with ethanol (300 cm$^3$) before drying at 80 ºC in a vacuum oven overnight. A three-step calcination sequence was utilised to form an alumina monolayer: the material was first heated to 250 °C for 1 h, then 400 °C for 1 h and finally 500 °C for 4 h (each ramp rate 1 °C.min$^{-1}$). Consecutive grafting cycles were undertaken employing an identical protocol in order to progressively build-up alumina monolayers over the silica surface, adjusting the quantities to maintain the initial Al:Si stoichiometry.

### Synthesis of hydrotalcite-coated MM-SBA-15 (HT/MM-SBA-15)

Magnesium methoxide solution (8-10 wt% in methanol) was added to Al-MM-SBA-15 (400 mg, dried for 1 h at 80 °C), at the minimum quantity to form a homogeneous paste on mixing. After stirring for 15 min, the mixture was dried under vacuum at 80 °C for 1 h to remove excess methanol. The surface Mg:Al atomic ratio was tuned by adjusting the volume of magnesium methoxide (10.8 cm$^3$ for the MM-SBA-15). The resulting material was calcined at 450 °C for 15 h under 20 cm$^3$.min$^{-1}$ $O_2$ (ramp rate 1 °C.min$^{-1}$). After cooling to room temperature under N2 (20 cm$^3$.min$^{-1}$), the powder was added to distilled water (50 cm$^3$ for every 300 mg of powder) in a 100 cm$^3$ round-bottomed pressure vessel and heated to 125 °C with stirring for 21 h. After cooling to room temperature, the final HT/MM-SBA-15 sample was filtered, washed with deionised water and dried in a vacuum oven overnight at 80 °C, before storage in a desiccator. This synthesis proved successful on the multi-gram scale. A conventional hydrotalcite reference material was prepared via our alkali-free, co-precipitation method from $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ precursors,[37] with the Mg: Al atomic ratio tuned to match that of the MM-SBA-15.

## Materials characterisation

Nitrogen porosimetry was undertaken on a Quantachrome Nova 1200 porosimeter. Samples were degassed at 120 °C for 2 h prior to analysis. Multi-point BET surface areas were calculated over the relative pressure range 0.01–0.3. Pore diameters and volumes were calculated applying either the t-plot or BJH methods to the desorption isotherm for relative pressures of 0.3-0.5 and 0.35 respectively. Powder XRD patterns were recorded on a PANalytical X'pertPro diffractometer fitted with an X'celerator detector and Cu Kα source for 2θ = 10–80° with a step size of 0.02°. The Scherrer equation was used to calculate HT crystallite sizes. XPS was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutraliser and magnetic focusing lens employing Al $K_\alpha$ monochromated radiation (1486.7 eV). Spectral fitting was performed using CasaXPS version 2.3.15. Base site densities were measured via $CO_2$ pulse chemisorption and subsequent temperature programmed desorption (TPD) on a Quantachrome ChemBET 3000 system coupled to an MKS Minilab QMS. Samples were outgassed at 120 °C under flowing He (120 cm$^3$.min$^{-1}$) for 1 h, prior to $CO_2$ titration at 40 °C and subsequent desorption under a temperature ramp of 8 °C min$^{-1}$. SEM analysis was carried out on a Carl Zeiss EVO SEM fitted with an Oxford Instruments energy dispersive X-ray (EDX) analyser employing Oxford Instruments Inca Software. Prior to analysis samples were uniformly dispersed over a carbon disc on an aluminium stub, and sputter coated with 90 : 10 mixture of gold and palladium to minimise charging. TGA was performed using a Stanton Redcroft STA780 thermal analyzer at heating rate of 10 °C.min$^{-1}$ under flowing He (20 cm$^3$.min$^{-1}$)

## Transesterification

The HT/MM-SBA-15 and conventional HT materials were tested as catalysts in the transesterification of triolein to form methyl trioleate (FAME) using a Radleys Starfish parallel reactor. Briefly, 50 mg of catalyst was added to 10 mmol of triolein using a 30:14:1 methanol:butanol:oil ratio; butanol was added as a co-solvent to help solubilise the triglyceride. In light of the significant differences in HT content between our conventional and SBA-15 coated materials, a common total mass of catalyst (rather than mass of hydrotalcite) was employed to ensure identical mixing characteristics within the reaction vessel. Reactions were carried out at 90 °C in a modified ACE™ 50 $cm^3$ round bottom pressure flask, with aliquots removed periodically from the reaction mixture for analysis on a Varian 450 GC with 8400 autosampler (programmable on-column injection onto a Phenomenex ZB-1HT column (15 m x 0.53 mm x 0.15 μm film thickness). Initial rates were calculated from the linear portion of the reaction profile during the first 60 min of the reaction. Turnover frequencies (TOFs) were determined by normalising rates to the total base site density from $CO_2$ chemisorption.

## Catalyst characterisation

### Porosimetry and powder X-ray diffraction:

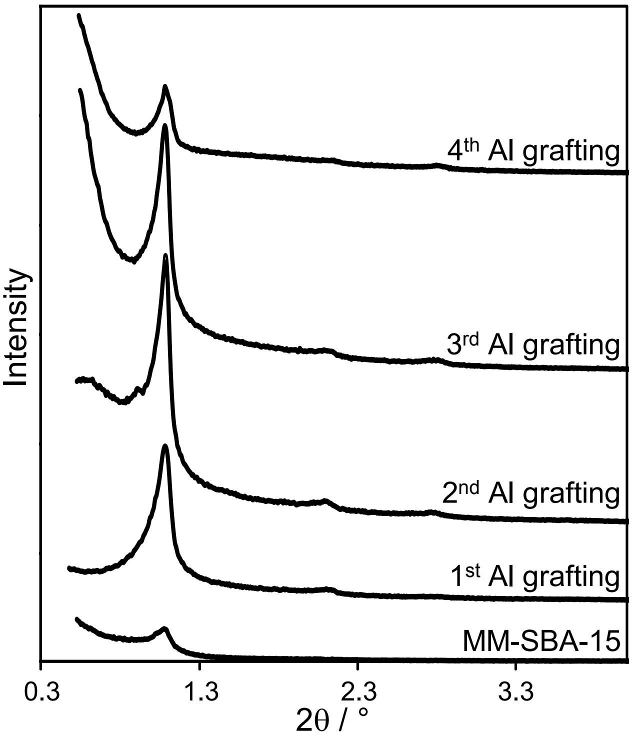

**Figure S1.** Low angle XRD patterns for parent MM-SBA-15 and alumina grafted variants as a function of grafting cycle (offset for clarity).

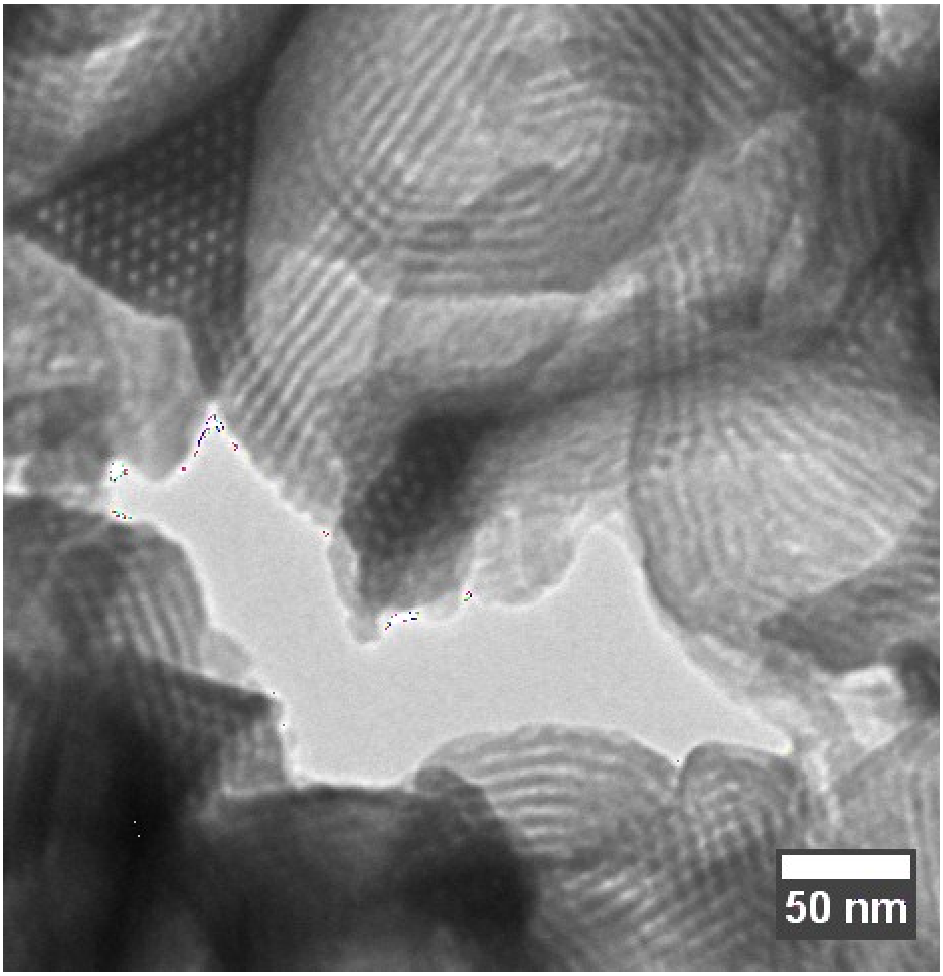

**Figure S2.** HRTEM of ordered mesopores within HT/MM-SBA-15 material.

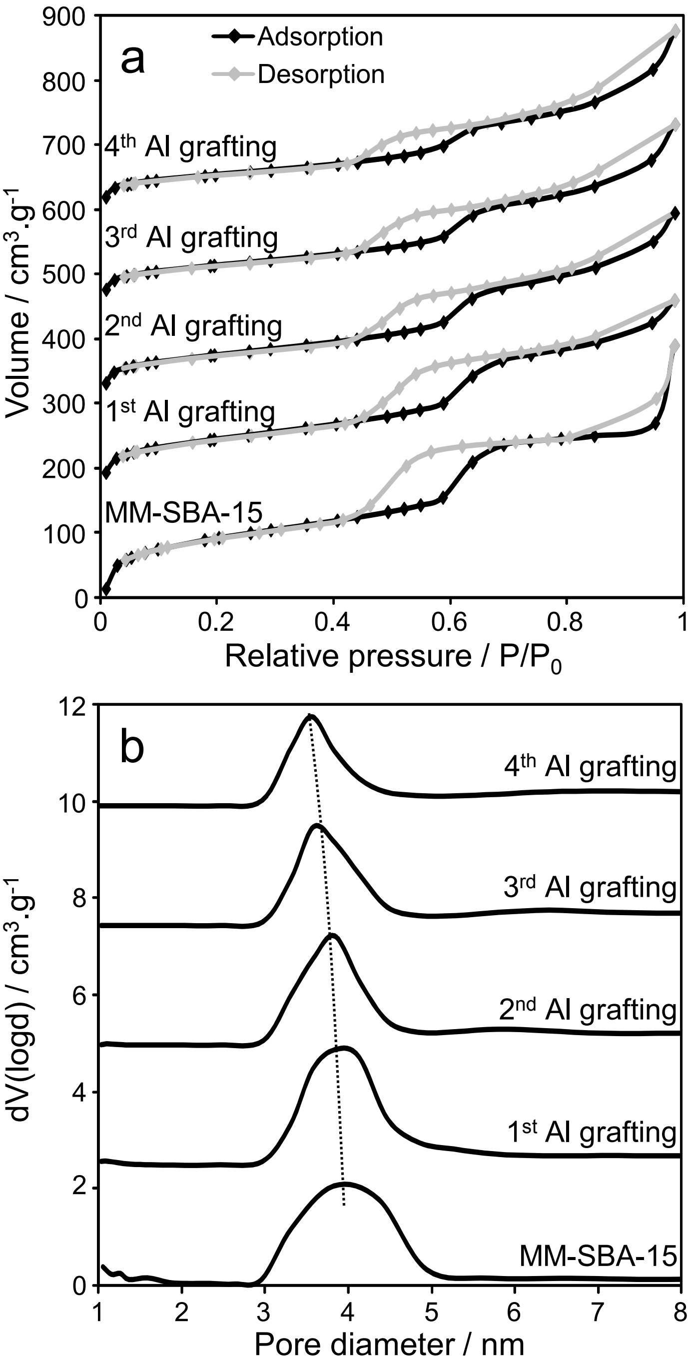

**Figure S3.** (a) $N_2$ adsorption-desorption isotherms and (b) BJH pore size distributions for parent MM-SBA-15 and alumina grafted variants as a function of grafting cycle (offset for clarity).

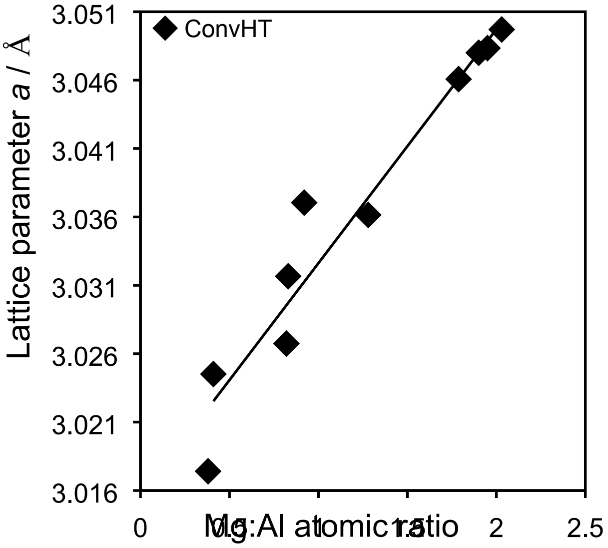

**Figure S4.** Proportionality between composition and unit cell (Vegard's Law) of Mg-Al hydrotalcites prepared via alkali-free co-precipitation.

Thermogravimetric analysis:

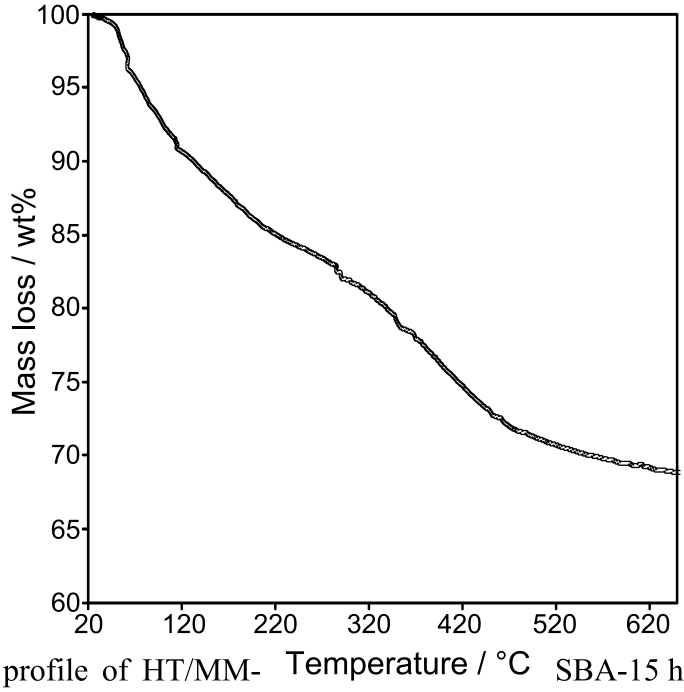

**Figure S5.** Thermogravimetric profile of HT/MM-SBA-15 hydrotalcite.

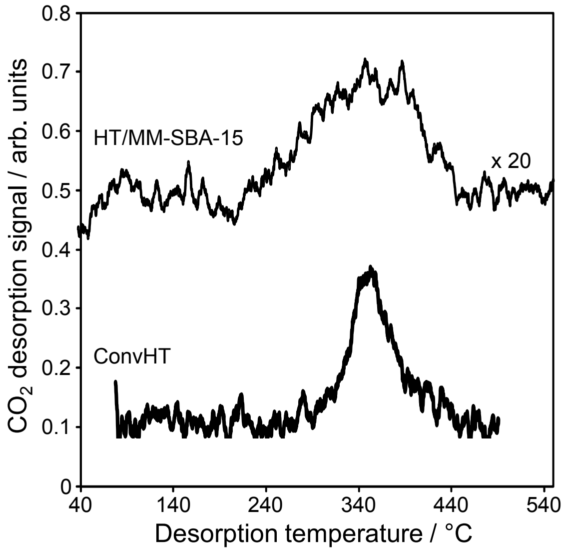

**Figure S6.** $CO_2$ temperature programmed desorption spectra for HT/MM-SBA-15 and a conventional HT standard.

**Catalyst transesterification**

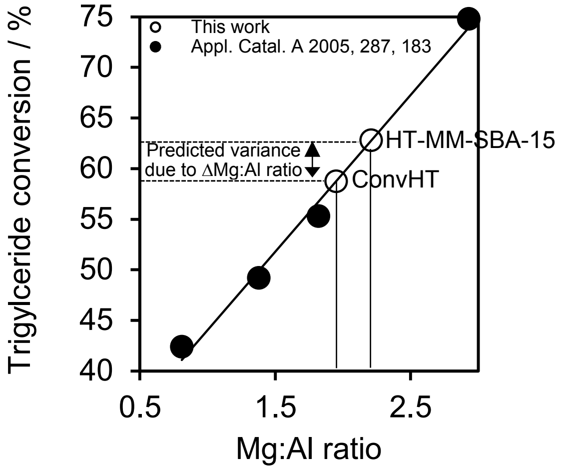

**Figure S7.** Tributyrin transesterification with MeOH dependence on bulk Mg:Al ratio for conventional co-precipitated bulk MgAl hydrotalcites.[1] Maximum predicted variance in triolein transesterification with MeOH between bulk ConvHT and HT/MM-SBA-15 materials extrapolated for present work.

**Table S1.** Porosimetry of Al-MM-SBA-15 precursor and HT/MM-SBA-15

| Material | Surface area[a] / $m^2.g^{-1}$ | Mesopore volume[b] / $cm^3.g^{-1}$ | Mesopore diameter[b] / nm |
|---|---|---|---|
| Al-MM-SBA-15 | 201 | 0.45 | 3.71 |
| HT/MM-SBA-15 | 246 | 0.47 | 3.66 |

[a]Evaluated by multi-point BET method. [b]BJH mesopore volume and pore diameter from the desorption isotherm.

1. D.G. Cantrell, L. J. Gillie, A.F. Lee, K. Wilson *Appl. Catal. A* **2005**, *287*, 183.