

Supporting Information

Better by design: nanoengineered macroporous hydrotalcites for enhanced catalytic biodiesel production

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TGA Analysis

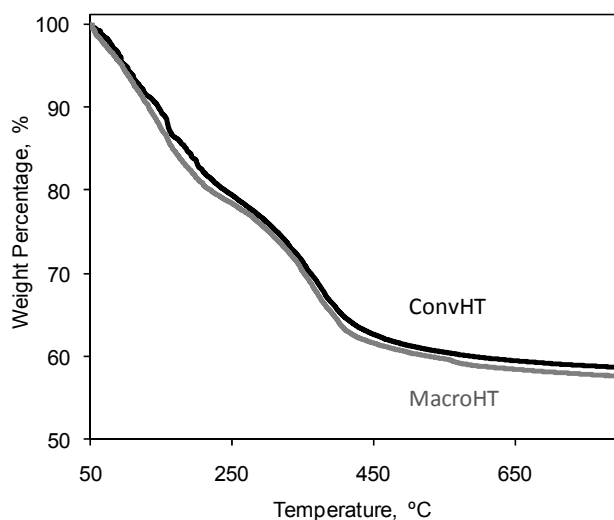


Fig. S1. TGA profiles for ConvHT and MacroHT.

Porosimetry

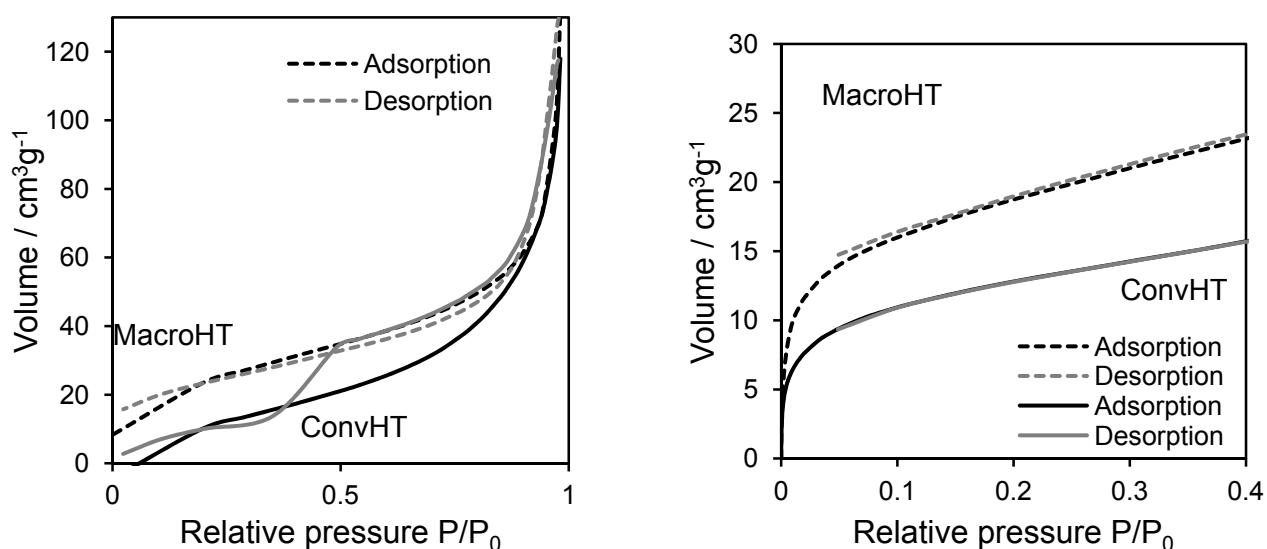


Fig. S2. N₂ adsorption-desorption isotherms for ConvHT and MacroHT.

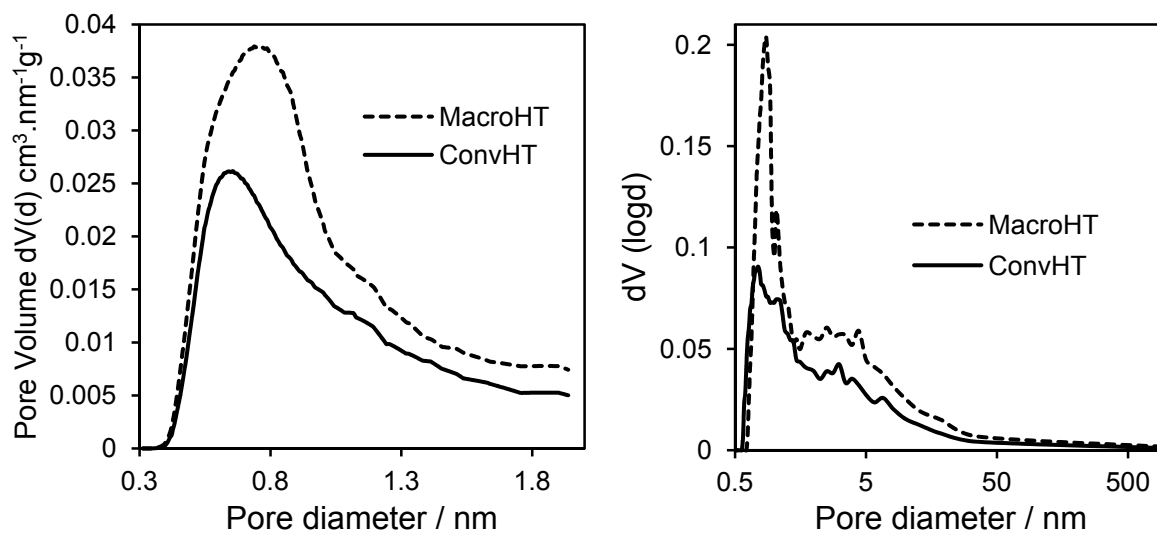


Fig. S3. (left) HK pore-size distributions, and (right) BJH pore-size distributions for ConvHT and MacroHT.

Table S1. Average pore diameters and total pore volumes (using the BJH method on the desorption branch) for ConvHT and MacroHT

Sample	Micropore volume (HK) cm^3/g	Total pore volume (BJH) cm^3/g	Fractional micropore volume / %	Average pore diameter, nm
ConvHT	0.0185	0.060	30	0.492
MacroHT	0.0271	0.091	30	0.838

XPS analysis

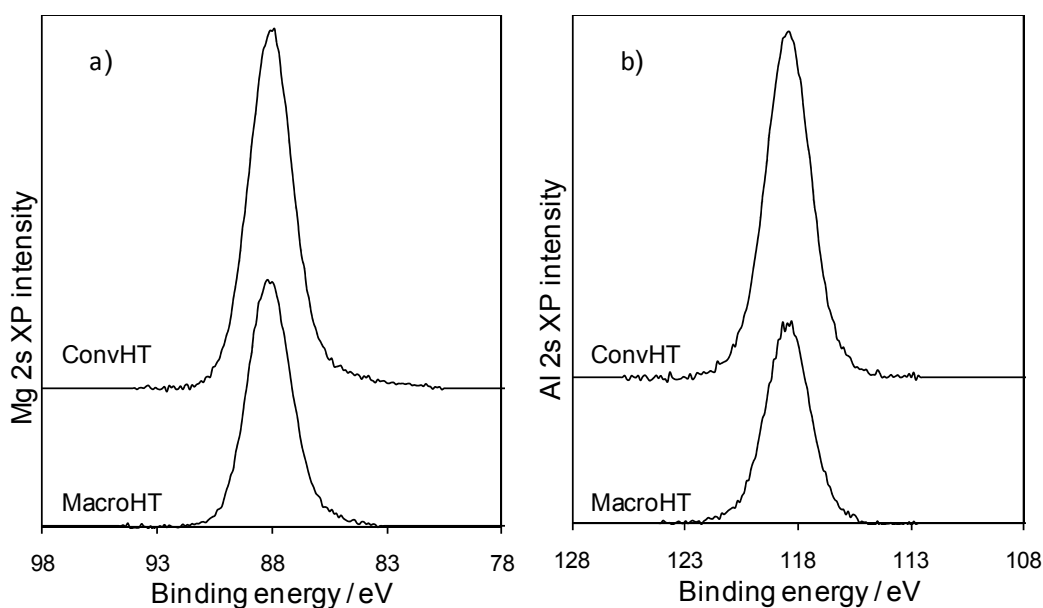


Fig. S3. XPS spectra showing a) the Mg 2s and b) the Al 2s chemical environments for ConvHT and MacroHT samples showing the presence of common surface species (base sites)

Benchmarking against homogeneously catalysed transesterification

The performance of ConvHT and MacroHT solid base catalysts was benchmarked against that of soluble Mg^{2+} ions derived from $Mg(OCH_3)_2$ towards the transesterification of tributyrin. In this experiment, the number of dissolved Mg ions (using 1 ml of a 6 mM) was chosen to precisely equal the number of solid base sites present in the ConvHT and MacroHT 50 mg catalyst charges (as derived by CO_2 titration). Figure S4 demonstrates that our solid base HT catalysts significantly outperform the related homogeneously catalysed reaction. In addition to proving the potential of heterogeneous catalysts for biodiesel production, this observation also evidences that the observed reactivity of our hydrotalcite catalysts does not arise from leached Mg.

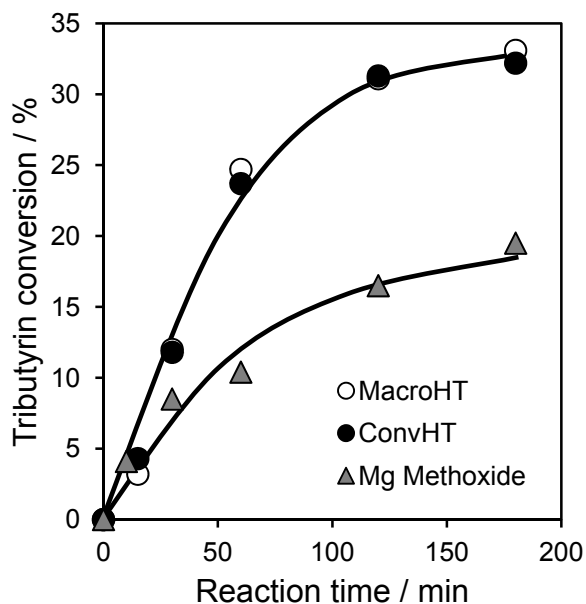


Fig. S4. Reaction profiles for ConvHT, MacroHT and soluble $Mg(OMe)_2$ in tributyrin transesterification with MeOH under standard reaction conditions.

Table S2. Comparative initial rates of tributyrin transesterification with MeOH for ConvHT and MacroHT

Catalyst	Initial rate / $mmol\ min^{-1}$
ConvHT	0.04
MacroHT	0.04
$Mg(OCH_3)_2$	0.02

Recycling tests

Tributyrin transesterification was performed under standard conditions. After 24 h reaction catalysts were recovered by filtration and repeated washing with methanol, then air dried and stored in a vacuum desiccator. Catalyst reactivation was performed utilising the same calcination and rehydration protocol described in the Experimental, and transesterification repeated. The performance of the re-used catalysts relative to their initial run is shown below; the MacroHT sample retained significantly more initial activity than the ConvHT, with the small loss observed associated with irreversibly adsorbed carbon deposits (XPS).

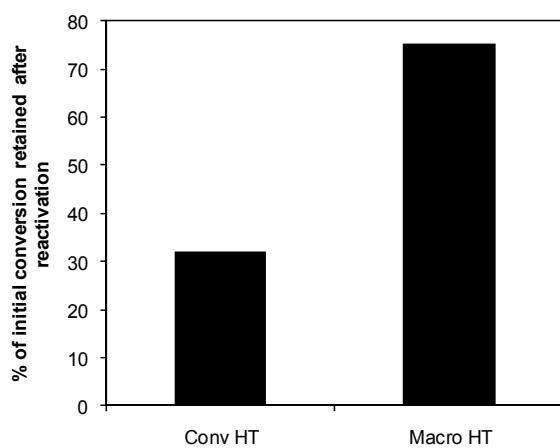


Fig. S5. Relative performance of re-activated ConvHT and Macro HT catalysts upon re-use for tributyrin transesterification.