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Pore-expanded SBA-15 sulfonic acid silicas for biodiesel synthesis†

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Here we present the first application of pore-expanded SBA-15 in heterogeneous catalysis. Pore expansion over the range 6–14 nm confers a striking activity enhancement towards fatty acid methyl ester (FAME) synthesis from triglycerides (TAG), and free fatty acid (FFA), attributed to improved mass transport and acid site accessibility.

Around 80% of the world's energy demands are currently met by fossil fuels. However, diminishing oil resources and rising concerns over the global impact of CO_2 emissions on climate change have led to a demand for sustainable energy supplies. Biodiesel sourced from non-food feedstocks has potential as an environmentally benign, alternative transportation fuel. Despite its early promise, societal concerns over land use, and political debate over 'eco-friendly' alternative energy technologies, have led to decreased biodiesel uptake in recent years. However, with ever rising crude oil costs, biodiesel manufacture is again viewed as a financially viable renewable fuel, and indeed recent reinstatement of tax credits by the US government is widely expected to increase biodiesel production.¹

Biodiesel comprises fatty acid methyl esters (FAME) of free fatty acids (FFAs) derived from various non-edible oils and animal fats, which are converted via reaction with liquid H₂SO₄ or soluble bases such as Na or K alkoxides to respectively esterify FFA or transesterify TAGs to their corresponding FAME.² Unfortunately, biodiesel purification remains an energy intensive step, generating vast quantities of aqueous waste containing alkali salts and impure glycerol by-product. Development of a heterogeneously catalysed process offering impurity-free fuel from low cost raw materials is essential to overcome these obstacles to commercialisation.³ Although numerous solid acids and bases have been explored for biodiesel synthesis,⁴ there have been minimal efforts to tailor catalyst porosity to optimise masstransport of the bulky and viscous C16-C18 TAGs or FFAs typical of plant oils. Conventional SBA-15 mesoporous silica derived catalysts have been previously examined in biodiesel synthesis⁵⁻⁸ possessing long, isolated parallel channels with

corresponding slow in-pore diffusion and catalytic turnover. We recently reported the benefits of hierarchical porous networks, incorporating 300–500 nm macropores to break up conventional mesoporous channels to act as rapid transport conduits to the active sites.⁹ However, the mesopores in this work remained close to the molecular dimensions of a typical TAG (~5 nm); hence, there is further scope for improving catalyst performance by also enlarging the mesopores themselves.

Porogens including trimethylbenzene,^{10,11} triethylbenzene or triisopropylbenzene¹² have been employed to swell the Pluronic P123 micelles used to produce SBA-15, enabling formation of mesopores with diameters 5 to 30 nm. Surprisingly, the potential catalytic applications of the resulting pore-expanded materials have not been exploited. The only previous reports of expanded mesopore catalysts are limited to MCM-41,¹³ and a composite of polystyrene sulfonic acid within an ultra-large pore SBA-15.¹⁴

While sulfonic acid-functionalized mesoporous materials have been previously tested in biodiesel synthesis,^{15–17} the pore sizes of such catalysts fall ≤ 6.5 nm and the relationship between pore diameter and mass transport properties remains unexplored. Here we present the first systematic report on the impact of pore diameter on the catalytic activity of sulfonic acid derivatised, pore-expanded SBA materials towards palmitic acid esterification, and the transesterification of tricaprylin and triolein, the latter a key component of commercial plant oil feedstocks *e.g.* palm, sunflower and jatropha.

Large pore SBA-15 variants (SBA-15-X) were obtained by adapting the approach of Fajula and co-workers11 as described in the ESI. Briefly, an appropriate amount of trimethylbenzene (TMB) was incorporated into the Pluronic P123/tetraethylortho-silicate (TEOS) micelle templating precursor solution. which was subsequently aged at different times (1-3 days) and temperatures (80-120 °C) in order to expand the integral micelles and silica pores following calcination. The successful synthesis of pore-expanded silica was first verified by low angle XRD, N₂ porosimetry and HRTEM. The N₂ adsorptiondesorption isotherms shown in Fig. 1 (inset) reveal that TMB does not perturb the isotherm type of the resulting silica, which remain Type IV. However, the hysteresis loop progressively shifts to higher relative pressures with both increasing aging time and temperature indicative of increasing pore size. The steep step and narrow hysteresis loops in the adsorption/desorption branches, evidence retention of the parent SBA-15 cylindrical, parallel pore channels. BJH analysis on the desorption branch (Fig. 1), shows that pores diameters

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Fig. 1 BJH pore size distribution from the desorption branch of the isotherm and (inset) isotherms for (a) SBA-15 and expanded pore analogues (b) SBA-15-8 and (c) SBA-15-14.

up to 14 nm can readily be achieved *via* this methodology. X-ray diffraction reveals all materials have good long range order with characteristic (100) diffraction peaks consistent with the *p6mm* hexagonal symmetry of SBA-15 (Fig. 2). A progressive shift of the d_{100} diffraction peak towards lower angle occurs across the series, associated with an increased *d*-spacing with aging temperature. This pore-expansion can also be observed by HRTEM (inset and Fig. S1, ESI†) which reveals highly-ordered periodic mesostructures, with pore diameters ~6, 8 and 14 nm. Additional physical parameters for the expanded SBA-15 series are given in Table S1, ESI†. The BET surface area decreased from 900 m²g⁻¹ (SBA-15) to 555 m² g⁻¹ (SBA-15-14), accompanied by a



Fig. 2 Low angle XRD of (a) SBA-15-6 and expanded pore analogues (b) SBA-15-8 and (c) SBA-15-14. Inset shows HRTEM of (i) SBA-15-6 and (ii) SBA-15-14.

corresponding increase in mesopore volume (from $1.08 \text{ cm}^3\text{g}^{-1}$ to 2.29 cm³ g⁻¹ respectively), upon pore-expansion, consistent with the geometric changes of the mesopore network. Our pore-expanded silicas were subsequently functionalised with sulfonic acid by mercaptopropyl trimethoxysilane (MPTS) grafting followed by oxidation with H₂O₂ (Scheme S1). This grafting route was adopted since it enables conformal derivatisation of the entire surface.¹⁸ XRD, porosimetry and HRTEM confirmed retention of the SBA-15 mesostructures during this process, while XPS showed a single S chemical environment (S 2p binding energy = 169.9 eV), indicative of total thiol conversion to sulfonic acid (Fig. S2, ESI[†]). The bulk and surface sulfonic acid loadings were determined via EDX and XPS respectively, revealing a decrease in bulk S content from 1.02 to 0.46 wt% across the series with falling surface area as expected (Table S2, ESI[†]). However, the overall SO₃H surface density remains ~ 0.21 nm⁻² across the series, similar to values reported for grafted sulfonic acid silicas, ^{19,20} and consistent with a constant surface silanol density upon pore expansion. Indeed, the S surface concentration determined by XPS remained ~ 0.45 wt% across our SBA-15 series, above that needed to maintain strong acid sites.¹⁸

The performance of the large pore, mesostructured sulfonic acid silicas was evaluated in the esterification of palmitic acid, and separate transesterification of tricaprylin and triolein, with methanol. These represent the two key steps necessary for the development of a heterogeneously catalysed biodiesel manufacturing process: the conversion of FFA impurities into FAME (Scheme 1); and subsequent transformation of the remaining TAGs to FAME. Steric factors and associated diffusion limitations render tricaprylin and triolein difficult to transesterify *via* conventional solid acid catalysts,²¹ making them interesting targets for mesostructured solid acids in their own right, with the C₁₈ triolein also the major component of olive oil, and thus an excellent model TAG with which to assess the potential benefits of mesopore expansion.

Reactions were performed under mild conditions to maintain relatively low conversions and enable kinetic analysis and were benchmarked against a commercial Amberlyst-15 acid catalyst. All samples were active for palmitic acid esterification, with ~25% conversion after 6 h (Table 1). Fig. 3 shows the corresponding Turnover Frequencies (TOFs, initial rates normalised per acid site) which indicate that <u>all</u> our SBA-SO₃H samples significantly outperform Amberlyst. Pore-expansion enhances TOF from 23 h⁻¹ for conventional sulfonic acid SBA-15 to 120 h⁻¹ for the analogous SBA-15-14 material.



Scheme 1 (a) FFA esterification and (b) TAG transesterification to FAME.

	C_{16} FFA esterification		$C_8 \& C_{18}^a TAG$ transesterification		
Catalyst	/%	$/h^{-1}$	/%	$/h^{-1}$	Ref
RSO ₃ H	23.2	23.4	2.1	3.3	This
SBA-15-6			0.1	0.04	work
RSO ₃ H	32.9	55.2	5.9	6.6	This
SBA-15-8			0.25	0.9	work
RSO ₃ H	33.5	120.2	6.7	11.7	This
SBA-15-14			0.3	1.1	work
Amberlyst ^d	31.3	2.6	0.4	0.04	
			0.4	0.04	
RSO ₃ H MM-SBA-4	55.4	35.6	2.5	7.8	9
Cs _{2.8} H _{1.2} SiW ₁₂ O ₄₀	76	100.6	11	12.5	22

^{*a*} C₁₈Triolein in italics; ^{*b*} After 6 hrs reaction; ^{*c*} Calculated per S site (based on bulk S content); ^{*d*} Amberlyst acid loading 4.3 mmol g^{-1}



Fig. 3 Reactivity of Amberlyst and sulfonic acid derivatised SBA-15-6; SBA-15-8 and SBA-15-14 catalysts in palmitic acid esterification and transesterification of tricaprylin and triolein.

Similar enhancement is seen in tricaprylin and triolein transesterification with increasing pore diameter across the series. We attribute the improved performance in both reactions to the greater accessibility of sulfonic acid sites resulting from larger mesopores. Table 1 compares conversions and TOFs of our pore-expanded SBA-15 sulfonic acids in esterification and transesterification, revealing they even outperform our previously reported hierarchical sulfonic acid silicas (RSO₃H-MM-SBA-4) and Cs_{2.8}H_{1.2}SiW₁₂O₄₀, suggesting that mesopore diffusion may have been only partially alleviated by macropore conduits in the former. Acid strength is another key parameter influencing activity in both esterification and transesterification.¹⁸ It is therefore interesting to note the similarities in TOFs with those for Cs_{2.8}H_{1.2}SiW₁₂O₄₀,²² which likely possesses similar acid strength $(-\Delta H(NH_3)_{ads})$ of 120-130 kJ mol⁻¹ vs. 133 kJ mol⁻¹ for grafted propylsulfonic acid SBA¹⁹).

The application of pore-expanded SBA-15 silicas in heterogeneous catalysis, in the present instance as solid acid catalysts, is reported for the first time. We demonstrate pore expansion confers > 3-fold increase in activity towards both C₁₆ FFA esterification and C₈/C₁₈ TAG transesterification *versus* conventional SBA-15, likely reflecting superior mass-transport of the bulky free fatty acid and triglycerides. We are currently undertaking molecular dynamic and Monte Carlo simulations to further optimise these pore-expanded silicas and assess the potential benefits of macropore integration to generate hierarchical pore-expanded networks. This work highlights the significant benefits in catalytic clean technologies achievable through careful nanoengineering of materials for the transformation of bulky biomass-derived feedstocks.

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