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Influence of alkyl chain length on sulfated zirconia catalysed batch and continuous esterification of carboxylic acids by light alcohols†‡§

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The impact of alkyl chain length on the esterification of C₂–C₁₆ organic acids with C₁–C₄ alcohols has been systematically investigated over bulk and SBA-15 supported sulfated zirconias (SZs). Rates of catalytic esterification for methanol with acetic acid are directly proportional to the sulfur content for both SZ and SZ/SBA-15, with the high dispersion of SZ achievable in conformal coatings over mesoporous SBA-15 conferring significant rate-enhancements. Esterification over the most active 0.24 mmol g_{cat}⁻¹ bulk SZ and 0.29 mmol g_{cat}⁻¹ SZ/SBA-15 materials was inversely proportional to the alkyl chain length of alcohol and acid reactants; being most sensitive to changes from methanol to ethanol and acetic to hexanoic acids respectively. Kinetic analyses reveal that these alkyl chain dependencies are in excellent accord with the Taft relationship for polar and steric effects in aliphatic systems and the enthalpy of alcohol adsorption, implicating a Langmuir–Hinshelwood mechanism. The first continuous production of methyl propionate over a SZ fixed-bed is also demonstrated.

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1. Introduction

Heterogeneous catalysis underpins sustainable chemical processes, enabling waste minimisation, improved product selectivity and thereby resource utilisation, in addition to lowering the energy required to convert raw materials and associated CO₂ emissions. Despite being central to the ‘12 principles of Green Chemistry’ first espoused by Anastas and Warner,¹ the discovery, design and development of tailored catalysts for clean chemical syntheses remains an area of great academic and commercial interest. Carboxylic acid esterification is of huge importance to the chemical industry for the production of solvents, fragrances and polymers, *e.g.* polyethylene terephthalate, acrylate esters, and cellulose acetate, yet largely employs processes developed at the turn of the century which still utilise corrosive and hazardous mineral acids (*e.g.* H₂SO₄, HCl, aryl sulphonic acids),² necessitating costly and energy intensive water treatments. In the context of Green Chemistry

the development of non-corrosive and recoverable solid acid catalysts for energy efficient (and continuous) esterification is therefore highly desirable to improve E-factors by circumventing the generation of copious amounts of inorganic waste typically produced.^{3,4} Solid acids based upon mesoporous oxides offer significant process advantages over microporous zeolites or acidic polymer resins, since the latter are ill-suited to bulky reactants which cannot readily access active sites within their frameworks. For example, propanoic acid esterification with methanol over Amberlyst-15 is 15 times slower than over mesoporous sulfonic acid silicas.⁵

Carboxylic acid esterification is also of growing importance in the context of renewable fuels, wherein concerns over depleting fossil fuel resources, climate change and CO₂ emissions are driving the quest for clean catalytic technologies for biofuels production from the conversion of (non-edible) lignocellulose and/or triacylglycerides to alkane fuels or biodiesel.^{6,7} Likewise, esterification of biomass derived platform chemicals,^{8,9} including lactic, levulinic, itaconic, succinic and furan dicarboxylic acid, offers a sustainable route to produce a diverse range of esters and polyesters for use as bio-based solvents, fuel additives or materials.^{10–12} However, despite these opportunities, significant technical hurdles exist to the use of such biomass feedstocks which limit their economic deployment.⁸

The availability of a well-defined solid acid catalyst capable of esterifying short (C₁–C₃) and long chain (C₁₂–C₂₀) organic acids is particularly important for biofuel synthesis. Pyrolytic

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†The authors dedicate this paper to Professor James H. Clark in honour of his 65th birthday and immense contributions to the field of green chemistry to date.

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§Electronic supplementary information (ESI) available: Sulfur loading analysis, temperature dependant propylamine desorption on TGA-MS, porosimetry isotherms, measurement of heat of adsorption, reaction profiles and TOFs, calculation of rate constant and Taft plots. See DOI: 10.1039/c6gc01089j



thermal decomposition of biomass, commonly used to generate liquid bio-oil for energy applications, produces an oil of low pH due to significant levels of C₁–C₃ organic acids. The corrosive nature of these bio-oils is detrimental for the lifetime of deoxygenation catalysts used in their downstream reforming, hence pre-treatment processes are required to neutralise their acidity and thereby improve oil stability.⁶ Similar pre-treatments are required to remove C₁₂–C₂₀ fatty acids from waste cooking, non-edible plant and algal oils to facilitate biodiesel production.³ Biodiesel typically comprises fatty acid methyl esters (FAMES) formed *via* the esterification and transesterification of free fatty acids (FFAs) and triacyl glycerides (TAGs) respectively.¹³ Commercial biodiesel production currently employs energy-intensive and environmentally unfriendly processes utilising homogenous base catalysts such as sodium or potassium methoxide.⁵ Such liquid catalysts are highly active for transesterification, but very sensitive to water and FFAs, with saponification during aqueous quench and neutralisation steps generating vast quantities of inorganic salt contaminated aqueous waste, which hinders biodiesel purification and results in a high E-factor for the process.^{5,14} Life-cycle calculations on biodiesel synthesis from soybean feedstock show that fuel purification and associated water treatment is the single most energy intensive step in biodiesel production, accounting for 87% of the total primary energy input.¹⁵ Reducing the production of contaminated water during biomass conversion processes is critical to minimise any negative impact on society.¹⁶

Various solid acid catalysts have been studied for carboxylic acid esterification, including sulfonic acid functionalised (hierarchical) mesoporous SBA-15,^{14,17–21} KIT-6⁵ and PMO¹³ silicas, Cs-exchanged heteropolyacids,^{22–26} tungstated zirconia,²⁷ zirconium phosphate^{28–30} and Nafion/SiO₂ composite (SAC-13),³¹ and sulphated zirconia (SZ).^{32–34} Of these solid acids, SZ is an attractive candidate because of its superacidic properties, low cost and good thermal stability.^{35–37} However, previous studies have either focused on use of bulk SZ for the esterification of short chain acids with methanol or ethanol, or the esterification of >C₁₀ fatty acids.^{36,38,39} While such bulk SZs are promising solid acid catalysts, their low surface areas present significant opportunities to improve efficiency through the development of highly porous and nanocrystalline SZ phases with tunable acidity. To date, the impact of sulfur loading and associated acid strength on catalytic esterification has not been systematically investigated, and is important for optimising both product yield and also catalyst stability.

Herein, we report on the application of two systematic families of bulk and highly dispersed SZs⁴⁰ (synthesised as conformal monolayers over an ordered mesoporous silica support) to the esterification of carboxylic acids in batch and continuous flow reactors. Alkyl chain length of both alcohol and acid influenced activity, reflecting a combination of steric and electronic effects and consistent with a bimolecular surface reaction. A first demonstration of the continuous liquid phase esterification of methanol with propanoic acid is also demonstrated for the most active SZ catalyst.

2. Experimental

Catalyst synthesis & characterisation

Bulk sulfated zirconia. The preparation of bulk sulfated zirconia with tunable acid loading has been previously reported elsewhere.⁴¹ Briefly, a series of SZ catalysts with different SO₄²⁻ loadings were prepared by impregnation of 50 g Zr(OH)₄ (MEL Chemicals – XZO 880/01) with 500 ml H₂SO₄(aq) of molarity 0.01–0.5 M. The slurry was stirred for 5 h at ambient temperature, filtered and dried at 80 °C overnight, and then calcined at 550 °C for 3 h. Catalysts were stored in air and used without pre-treatment.

SZ grafted SBA-15. High surface area SBA-15 supported sulphated zirconia catalysts were prepared following the method reported in our previous work.⁴² Briefly, 10 g of SBA-15 (prepared *via* the original method of Zhao *et al.*⁴³) was dried at 300 °C for 4 h, then cooled to 100 °C and added to a solution of 58.5 g of 70% zirconium propoxide in propanol (Sigma-Aldrich) in 300 mL of anhydrous hexane. The amount of zirconium precursor was calculated on the basis of the number of surface hydroxyl groups on SBA-15 (determined from thermal gravimetric analysis). The reaction mixture was refluxed at 69 °C overnight, filtered, and washed three times with hexane to remove any unreacted precursor. The material was subsequently rehydrated in 300 mL of deionized water under stirring for 4 h to fully hydrolyse any residual propoxide groups. Finally, the catalyst was filtered and dried at 80 °C overnight. This procedure was repeated to produce SBA-15 coated with a nominal second and third monolayer of zirconia. Sulfation of ZrO₂/SBA-15 materials was achieved *via* their immersion in aqueous sulfuric acid (10 mL acid solution per g sample, H₂SO₄ concentrations spanning 0.015–0.25 M) for 5 h, after which samples were filtered and dried overnight at 80 °C. The resulting materials were activated by calcination at 550 °C in static air for 3 h.

All catalysts were fully characterised by N₂ physisorption, CHNS elemental analysis, acid site titration by propylamine chemisorption/TPD. Heats of adsorption of methanol, ethanol and 1-propanol on 0.05SZ were measured using a fully-automated Surface Measurement Systems Ltd Inverse GC system, with surface properties determined according to literature methods.^{44,45} Full details of the experimental procedures and equipment are given in the ESI.†

Catalytic esterification reactions

Batch esterification was performed at 60 °C using a Radleys Carousel Reactor Station using 150 mmol alcohol (methanol, ethanol, 1-propanol or 1-butanol), 5 mmol of propanoic (C₃), hexanoic (C₆), lauric (C₁₂) or palmitic (C₁₆) acid, with 0.5 mmol of dihexyl ether (as an internal standard) and 25 mg Bulk SZ or 50 mg SZ/SBA-15.

Continuous flow esterification of propanoic acid and methanol was conducted at 60 °C using a commercial Uniqsis FlowSyn reactor. Briefly, 75 mg catalyst was diluted with quartz beads (Sigma Aldrich, mesh size = 325), and packed within a 10 mm i.d. × 100 mm OMNIFIT® glass column to give a total



bed volume of 1.7 cm³. A liquid stream of methanol (150 mmol) and propanoic acid (5 mmol) was then delivered to the packed bed at flow rates between 0.1 to 1 cm³ min⁻¹. Samples were collected periodically for analysis by GC. Full details of the reaction conditions and analytical procedure are given in the ESI.†

3. Results and discussion

Catalyst characterisation

Table 1 and Fig. S1–S4† summarise the physicochemical properties of the bulk SZ and SZ/SBA-15 catalysts employed in this study.^{40,41}

Bulk SZ samples possessed a relatively low BET surface area in the range of 140 to 200 m² g⁻¹ typical of non-porous sulfated zirconia catalysts. Mesoporous SZ/SBA-15 catalysts with surface areas between 430 and 490 m² g⁻¹ are consistent with previously reported materials.⁴² CHNS analysis and quantification of acid sites by propylamine adsorption/TGA-MS revealed that for bulk SZ the sulfur and acid site loading increased monotonically with the concentration of impregnating H₂SO₄ solution up to 0.25 M. While the sulfur content increased further for higher [H₂SO₄], the acid site loading reached a plateau due to the formation of multilayer sulfate compounds which do not contribute to the acidity.⁴¹ The sulfur and acid site loadings of the SZ/SBA-15 series likewise increased with [H₂SO₄] up to ~0.1 M before reaching a plateau when the surface saturated at ~0.17 M H₂SO₄. Previous NH₃ calorimetry on these samples has shown that while increasing the S loading from 0 to 1.8 wt% enhanced the acid strength of bulk SZ, further increases in S loading did not affect the acid strength, consistent with the formation of SO₄ multilayers at this point. This is also reflected in the peak propene desorption temperature for propylamine decomposition (Fig. S2†) which decreases from 440 °C to 425 °C with [H₂SO₄], consistent with increased acid strength. The acid strengths of the SZ/SBA-15 series were comparable to the highest loading bulk

SZ catalysts, and exhibit a weak dependence on SO₄ content; suggesting that surface Zr⁴⁺ sites are more readily polarised in conformal SZ coatings, even at the lowest SO₄²⁻ loadings.

Catalyst reactivity

Bulk versus dispersed SZ. To minimise mass transport limitations, esterification of the short chain acetic acid with methanol was first investigated in order to establish the role of SO₄²⁻ content on reactivity over both SZ families. Fig. 1 shows the resulting Zr normalised initial rates as a function of impregnating [H₂SO₄] concentration, which shows an initial increase in activity for both catalyst families with [H₂SO₄]. In general, SZ/SBA-15 was twice as active as its bulk SZ counterpart, attributed to the improved dispersion of the supported materials and attendant higher surface sulfate density. Both families exhibited maximum activity for materials synthesised with 0.05 M H₂SO₄, reflecting a combination of increased acid site

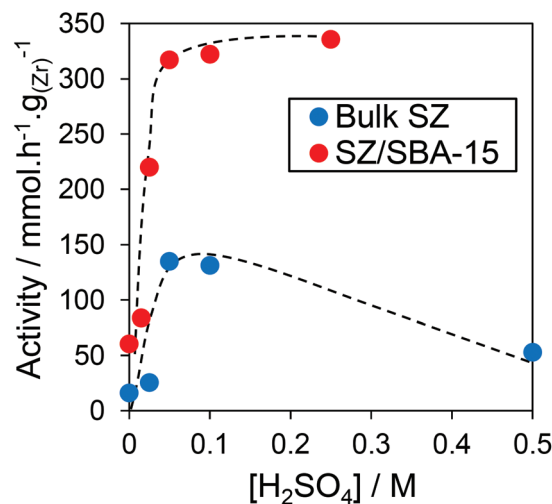


Fig. 1 Zr normalised initial reaction rates for acetic acid esterification with methanol over SZ and SZ/SBA-15 as a function of [H₂SO₄] impregnating solution.

Table 1 Physical properties of SZ and SZ/SBA-15 catalysts

Catalyst	Surface area ^a /m ² g ⁻¹	S loading ^b /wt%	Acid site loading ^c /mmol g ⁻¹	-ΔH _{ads} (NH ₃) ^d /kJ mol ⁻¹
ZrO ₂	93	0.00	0.03	85
0.015SZ	142	0.25	0.06	91
0.025SZ	175	0.53	0.11	99
0.05SZ	189	1.09	0.24	102
0.075SZ	175	1.49	0.33	115
0.1SZ	203	1.80	0.37	115
0.25SZ	194	2.24	0.36	115
0.5SZ	118	2.53	0.24	115
ZrO ₂ /SBA-15	450	0.00	0.15	112
0.015SZ/SBA-15	433	0.48	0.20	113
0.025SZ/SBA-15	445	0.78	0.22	114
0.05SZ/SBA-15	463	1.52	0.27	114
0.1SZ/SBA-15	390	1.74	0.29	121
0.17SZ/SBA-15	489	2.16	0.29	—
0.25SZ/SBA-15	441	2.10	0.32	116

^a BET. ^b CHNS. ^c Propylamine TGA-MS. ^d NH₃ calorimetry.



strength and concentration up to completion of a sulfate monolayer over SBA-15. The rate-limiting step in esterification is generally accepted to be nucleophilic attack of the alcohol on the carbenium ion formed through proton donation to the acid,⁴⁶ thus the increase acid strength across the series is expected to impact on the efficiency of carbenium ion formation and observed catalyst activity. Similar albeit less dramatic variations were also observed for longer chain acids and alcohols (Fig. S5–S10§). It is interesting to note for all reactions that a high activity was retained for SZ/SBA-15 for S contents >2 wt%, whereas that of the analogous bulk SZ decreased. This decrease coincides with the loss in surface area and crystallinity of the bulk systems (Table 1) following impregnation with >0.25 M [H₂SO₄] used to achieve the highest degree of sulfation.^{40,41}

Effect of alcohol and acid alkyl chain length. Steric and electronic effects in esterification were subsequently investigated for the optimum 0.05 M bulk SZ catalyst by varying both the acid and alcohol chain length. Fig. 2 shows the variation of Turnover Frequency (TOF) for propanoic acid esterification with C₁–C₄ alcohols, and of C₂–C₁₆ acids with methanol. In both cases, TOFs were strongly dependent upon the reactant size, with methanol three times more active than ethanol for propanoic acid esterification, and acetic acid twice as reactive as propanoic acid in their esterification with methanol. Increasing either alcohol or acid chain length beyond C₂ or C₆ respectively had little further impact. 0.05 SZ/SBA-15 exhibited a similar trend in reactivity with acid chain length, albeit with slightly lower TOFs, which may be arise from in-pore diffusion limitations.

The preceding results are consistent with a Langmuir–Hinshelwood bimolecular surface reaction model (Scheme 1).⁴⁷

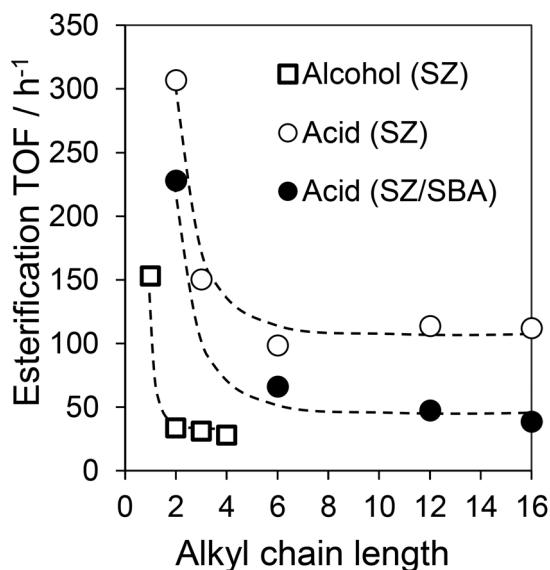
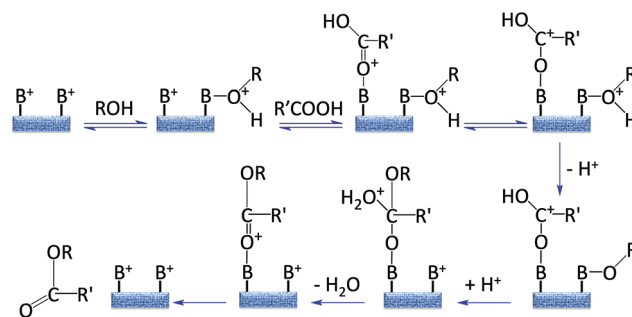


Fig. 2 TOFs for propanoic acid esterification with different alcohols over bulk 0.05SZ, and of C₂–C₁₆ acids with methanol over bulk 0.05SZ and 0.05SZ/SBA-15 catalysts.



Scheme 1 Mechanism of esterification over Brønsted acid (B⁺) sites of a sulfated zirconia catalyst. (Adapted from ref. 47.)

For this two site mechanism, coordination of the alcohol (*via* the hydroxyl oxygen) and the organic acid (*via* the carbonyl oxygen to form a carbocation) is required at adjacent Brønsted acid sites. The nucleophilic species generated upon deprotonation of the alcohol OH can then attack the carbocation to generate a tetrahedral intermediate which finally eliminates water to form the ester. Based on this proposed reaction mechanism, the lower activity of longer chain alcohols/acids is in accordance with previous observations,^{48,49} and can be attributed to polar and steric effects⁵⁰ in the aliphatic systems, and is well described by the Taft relationship as shown in Fig. S11.§ The gradient of the plot of $\log(k/k(\text{CH}_3))$ versus polar substituent (σ^*) or steric substituent constant (E_s) gives rise to the sensitivity factors for the reaction towards polar (ρ) or steric effects (δ) respectively. Fig. S11§ shows that ρ is >1 suggesting the reaction accumulates negative charge in the transition state which is accelerated by electron withdrawing groups, while δ is also positive indicating steric effects are greater in the transition state, with increased in steric bulk leading to decreased reaction rate. While such steric and polar effects dictate activity for short chain acids, for long chain fatty acids diffusion limitation and reduced accessibility of acid sites may also contribute to decreased TOF.

For alcohols, enhanced electron-donating properties with increased alkyl chain length are expected to destabilise the protonated transition state, explaining the concomitant decrease in esterification rate. Inverse gas chromatography measurements (Fig. S12§) also demonstrate that the adsorption enthalpy of C₁–C₃ alcohols on bulk SZ also decreases linearly with alkyl chain length (and pK_a) (Fig. 3). Hence, the higher reactivity of shorter chain alcohols can be understood in terms of their weaker adsorption relative to more strongly bound C₃ alcohols (of higher pK_a), which favour alkoxide formation and concomitant blocking of catalytic sites.

Larger, more sterically-demanding alcohols may also experience limited accessibility to protonated (or activated) carboxylates, likewise hindering catalytic turnover, as reported previously for the esterification of primary secondary and tertiary alcohols over bulk SZ wherein activity decreased from 1° > 2° > 3° alcohols.³⁶ The relative insensitivity of TOFs for longer chain alcohols is in agreement with studies of lauric acid esterification with C₁–C₆ alcohols,³⁶ although the study by



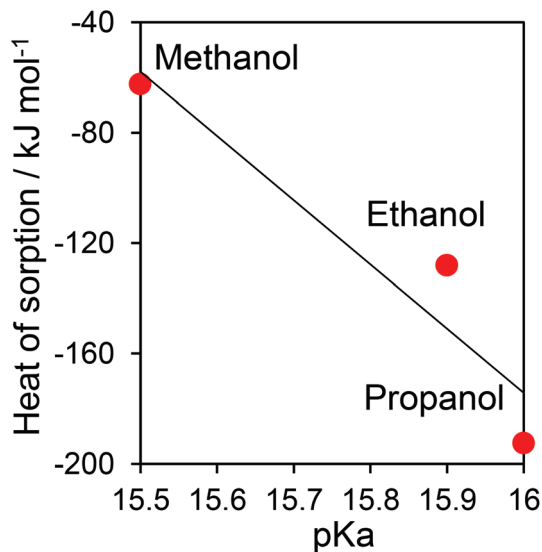


Fig. 3 Heat of adsorption of alcohols on 0.05SZ as a function of alcohol pK_a .

Greca and co-workers observed the same activity for methanol as longer chain alcohols (possibly a consequence of their lower alcohol : acid ratio of 1 : 1 and higher reaction temperature of 133 °C).

In the case of carboxylic acids, the inductive effect increases with chain length, with increases in the electron-donating ability of the acid, favouring protonation of the carboxylate oxygen. However, as a consequence, the electrophilicity of the carbonyl carbon is lowered, and hence the rate-limiting nucleophilic attack by an alcohol becomes disfavoured. This so called 'steric effect' increases with alkyl chain length of the carboxylic acid, and is widely assumed to dictate the reactivity of carboxylic acids in acid-catalysed esterification.^{50–52} Our observations in Fig. 2 are also consistent with the work of Liu *et al.*⁵⁰ who investigated the effect of alkyl chain length on FFA esterification with methanol using sulfuric acid and a commercial Nafion/silica composite (SAC-13). Thus, for acids $>C_6$ it seems likely that esterification is rate-limited not only by restricted access to active sites.

Table 2 summarises the conversions and initial rates of the esterification of all saturated organic acids explored, along with functional levulinic acid and unsaturated oleic and linoleic acids with methanol, to test the versatility of the 0.05SZ in esterification reactions of relevance to biomass conversion (Fig. S13[†]). It is interesting to note that under these mild conditions conversion of both oleic and linoleic acid is comparable to saturated palmitic acid suggesting that unsaturation is not detrimental to performance. The conversion of levulinic acid conversion also compares favourably to literature reports for SZ in levulinic acid esterification despite being under such mild conditions.^{53,54}

Continuous flow esterification. The ability to conduct esterification under continuous flow is highly desirable to increase process efficiency and facilitate the translation of catalytic

Table 2 Esterification of various carboxylic acids with methanol over 0.05SZ at 60 °C

Acid	6 h conversion ^a /%	Initial rate/mmol h ⁻¹
Acetic acid	75.2	2.07
Propanoic acid	67.9	1.01
Hexanoic acid	51.3	0.77
Lauric acid	53.6	0.77
Palmitic acid	40.4	0.75
Oleic acid	35.7	0.32
Linoleic acid	46.3	0.61
Levulinic acid	67.0	1.5

^a Ester selectivity >99%.

processes from laboratory to industrial scale.⁵⁵ We therefore explored whether the excellent activity of the optimum bulk 0.05SZ catalyst for the batch esterification of propanoic acid with methanol could be mirrored in a fixed bed continuous flow microreactor. Despite the commercial significance of esterification to the global chemicals sectors, and popularity of SZ as a solid acid catalyst, the only literature reports of continuous esterification using SZ are limited to the esterification of soybean oil⁵⁶ or octanoic acid.^{56,57} This may reflect concerns regarding the stability of commercial SZ catalysts towards SO_4^{2-} leaching in aqueous/polar environments.⁵⁸

The influence of residence time (τ) on propanoic acid conversion was first investigated (Fig. 4A). A monotonic rise in acid conversion was observed as the residence time was increased from $\tau = 4$ to 19 min, reaching a maximum of 0.55 mmol h⁻¹ g_(cat)⁻¹ for a residence time of 17.3 min, with single pass conversions reaching 45% and methyl propanoate selectivity $\geq 98\%$. The maximum acid conversion may be limited by poor mass-transport and the resulting accumulation of ester and water products at the catalyst surface for longer residence times, displacing the reaction equilibrium. Catalyst deactivation can be a significant barrier to the commercialisation of solid acid catalysts, with sulfate leaching and irreversible water adsorption often reported responsible for the deactivation of SZ catalysts.^{33,58} An extended propanoic acid esterification reaction was therefore performed to probe catalyst stability, employing a long residence time ($\tau = 17.3$ min) in order to maximise reactant–catalyst contact. Fig. 4B shows the resulting TOFs for continuous flow *versus* batch esterification. In batch, the TOF fell continuously from a high initial value of 175 after 1 h to only 80 after 6 h. This activity loss will certainly reflect consumption of the acid, but may also be conflated with displacement of the equilibrium by reactively-formed water and/or deactivation. In contrast, continuous esterification revealed an extremely stable and high TOF of 140 (with $\geq 98\%$ ester selectivity) throughout the 6 h reaction, evidencing excellent catalyst stability, and discounting deactivation as the cause of the poor longer term batch performance. Furthermore post reaction analysis of the reaction medium and catalyst by CHNS revealed no evidence for SO_4 loss. It seems likely that literature reports of sulfate leaching from SZ are a consequence



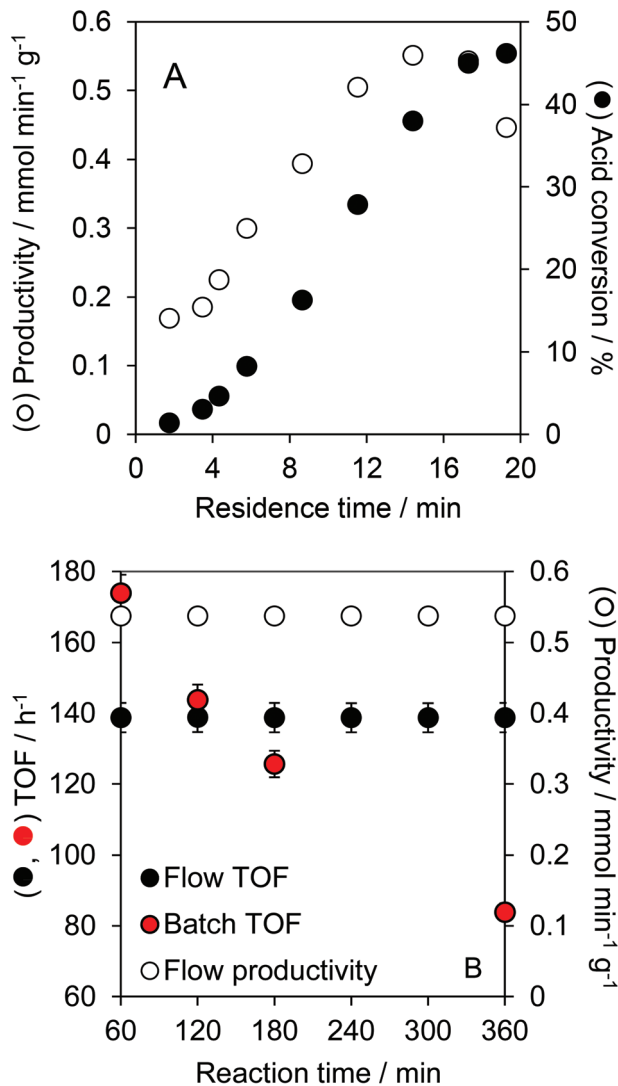


Fig. 4 (A) Influence of residence time on propanoic acid esterification with methanol over 0.05SZ. Reaction conditions: 65 mg catalyst, 0.1–1 cm³ min⁻¹ of 150 mmol MeOH/5 mmol propanoic acid, 60 °C. (B) Comparison of batch and flow esterification of propanoic acid and methanol over 0.05SZ. Reaction conditions: 75 mg catalyst, 150 mmol MeOH/5 mmol propanoic acid (stirred or flowed at 0.1 cm³ min⁻¹), 60 °C.

of the higher sulfuric acid concentrations (typically >0.25 M)⁵⁹ employed in their synthesis, which may leave significant unstable sulfoxy species following calcination⁶⁰ that are more susceptible towards leaching than our optimum SZ catalyst prepared with only 0.05 M H₂SO₄; control over the surface sulfate density may thus be integral to SZ stability.

Conclusions

Families of bulk and mesoporous silica supported SZ catalysts have been synthesised with variable sulfate loadings and investigated for the esterification of acetic acid with methanol.

Esterification activity increased with sulfate loading over both families, reaching a maximum for acid site loadings of 0.3 mmol g⁻¹, attained following impregnation by dilute 0.05 M H₂SO₄. SZ/SBA-15 catalysts were generally twice as active as their bulk counterparts when normalised to the Zr content reflecting superior sulfate dispersion throughout the high area mesopore network. Esterification activity over the optimal SZ and SZ/SBA-15 catalysts exhibits a pronounced dependence on the alkyl chain length of both acid and alcohol reactants, notably on switching from methanol to ethanol and acetic to propanoic acids. The dependences of both aliphatic alcohol and acid or polar and steric substituents follow a Taft relationship, which indicate reduced steric bulk or addition of electron withdrawing groups to aliphatic chain (**R**), of the alcohol (**RCOH**) or acid (**RCOOH**) increases the reaction rate.

Continuous esterification of propanoic acid with methanol under mild conditions is successfully demonstrated for the first time over a fixed-bed of bulk SZ, affording extremely stable operation with good conversion and excellent selectivity to methyl propanoate, and evidencing negligible S leaching.

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References

- 1 P. T. Anastas and J. C. Warner, *Green chemistry: theory and practice*, Oxford University Press, 2000.
- 2 G. D. Yadav and P. H. Mehta, *Ind. Eng. Chem. Res.*, 1994, **33**, 2198–2208.
- 3 K. Wilson and A. F. Lee, *Catal. Sci. Technol.*, 2012, **2**, 884–897.
- 4 R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273–1283.
- 5 C. Pirez, J.-M. Caderon, J.-P. Dacquin, A. F. Lee and K. Wilson, *ACS Catal.*, 2012, **2**, 1607–1614.
- 6 L. Ciddor, J. A. Bennett, J. A. Hunns, K. Wilson and A. F. Lee, *J. Chem. Technol. Biotechnol.*, 2015, **90**, 780–795.
- 7 A. F. Lee, J. A. Bennett, J. C. Manayil and K. Wilson, *Chem. Soc. Rev.*, 2014, **43**, 7887–7916.
- 8 K. Wilson and A. F. Lee, *Philos. Trans. R. Soc., A*, 2016, **374**, 20150081.
- 9 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489.



- 10 F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.*, 2010, **122**, 5642–5646.
- 11 M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina and B. F. Sels, *Energy Environ. Sci.*, 2013, **6**, 1415–1442.
- 12 J. H. Clark, V. Budarin, T. Dugmore, R. Luque, D. J. Macquarrie and V. Strelko, *Catal. Commun.*, 2008, **9**, 1709–1714.
- 13 C. Pirez, M. T. Reche, A. F. Lee, J. C. Manayil, V. C. dos-Santos and K. Wilson, *Catal. Lett.*, 2015, **145**, 1483–1490.
- 14 J. Dhainaut, J.-P. Dacquin, A. F. Lee and K. Wilson, *Green Chem.*, 2010, **12**, 296–303.
- 15 J. Sheehan, V. Camobreco, J. Duffield, M. Graboski and H. Shapouri, *An overview of biodiesel and petroleum diesel life cycles*, National Renewable Energy Laboratory, Golden, 1998.
- 16 K. Mulder, N. Hagens and B. Fisher, *Ambio*, 2010, **39**, 30–39.
- 17 I. K. Mbaraka, D. R. Radu, V. S. Y. Lin and B. H. Shanks, *J. Catal.*, 2003, **219**, 329–336.
- 18 J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias and D. Briones, *Energy Fuels*, 2008, **23**, 539–547.
- 19 S. Garg, K. Soni, G. M. Kumaran, R. Bal, K. Gora-Marek, J. K. Gupta, L. D. Sharma and G. M. Dhar, *Catal. Today*, 2009, **141**, 125–129.
- 20 J. P. Dacquin, A. F. Lee, C. Pirez and K. Wilson, *Chem. Commun.*, 2012, **48**, 212–214.
- 21 C. Pirez, A. F. Lee, J. C. Manayil, C. M. A. Parlett and K. Wilson, *Green Chem.*, 2014, **16**, 4506–4509.
- 22 A. Alsalmé, E. F. Kozhevnikova and I. V. Kozhevnikov, *Appl. Catal., A*, 2008, **349**, 170–176.
- 23 Y. Leng, J. Wang, D. Zhu, Y. Wu and P. Zhao, *J. Mol. Catal. A: Chem.*, 2009, **313**, 1–6.
- 24 V. Dufaud, F. Lefebvre, G. P. Niccolai and M. Aouine, *J. Mater. Chem.*, 2009, **19**, 1142–1150.
- 25 K. Narasimharao, D. R. Brown, A. F. Lee, A. D. Newman, P. F. Siril, S. J. Tavener and K. Wilson, *J. Catal.*, 2007, **248**, 226–234.
- 26 L. Pesaresi, D. R. Brown, A. F. Lee, J. M. Montero, H. Williams and K. Wilson, *Appl. Catal., A*, 2009, **360**, 50–58.
- 27 D. E. López, K. Suwannakarn, D. A. Bruce and J. G. Goodwin Jr., *J. Catal.*, 2007, **247**, 43–50.
- 28 K. Ngaosuwan, X. Mo, J. G. Goodwin Jr. and P. Praserthdam, *Appl. Catal., A*, 2010, **380**, 81–86.
- 29 K. Ngaosuwan, X. Mo, J. G. Goodwin and P. Praserthdam, *Top. Catal.*, 2010, **53**, 783–794.
- 30 K. N. Rao, A. Sridhar, A. F. Lee, S. J. Tavener, N. A. Young and K. Wilson, *Green Chem.*, 2006, **8**, 790–797.
- 31 J. A. Melero, J. Iglesias and G. Morales, *Green Chem.*, 2009, **11**, 1285–1308.
- 32 J. Ni and F. C. Meunier, *Appl. Catal., A*, 2007, **333**, 122–130.
- 33 D. E. López, J. G. Goodwin Jr., D. A. Bruce and S. Furuta, *Appl. Catal., A*, 2008, **339**, 76–83.
- 34 X.-R. Chen, Y.-H. Ju and C.-Y. Mou, *J. Phys. Chem. C*, 2007, **111**, 18731–18737.
- 35 M. A. Ecomier, K. Wilson and A. F. Lee, *J. Catal.*, 2003, **215**, 57–65.
- 36 M. L. Grecea, A. C. Dimian, S. Tanase, V. Subbiah and G. Rothenberg, *Catal. Sci. Technol.*, 2012, **2**, 1500–1506.
- 37 A. A. Kiss, A. C. Dimian and G. Rothenberg, *Adv. Synth. Catal.*, 2006, **348**, 75–81.
- 38 K. Saravanan, B. Tyagi and H. C. Bajaj, *Catal. Sci. Technol.*, 2012, **2**, 2512–2520.
- 39 D. Rattanaphra, A. P. Harvey, A. Thanapimmetha and P. Srinophakun, *Renewable Energy*, 2011, **36**, 2679–2686.
- 40 A. Osatiashtiani, A. F. Lee, M. Granollers, D. R. Brown, L. Olivi, G. Morales, J. A. Melero and K. Wilson, *ACS Catal.*, 2015, **5**, 4345–4352.
- 41 A. Osatiashtiani, A. F. Lee, D. R. Brown, J. A. Melero, G. Morales and K. Wilson, *Catal. Sci. Technol.*, 2014, **4**, 333–342.
- 42 G. Morales, A. Osatiashtiani, B. Hernandez, J. Iglesias, J. A. Melero, M. Paniagua, D. Robert Brown, M. Granollers, A. F. Lee and K. Wilson, *Chem. Commun.*, 2014, **50**, 11742–11745.
- 43 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552.
- 44 M. C. Gutierrez, J. Rubio, F. Rubio and J. L. Oteo, *J. Chromatogr., A*, 1999, **845**, 53–66.
- 45 H. E. Newell, G. Buckton, D. A. Butler, F. Thielmann and D. R. Williams, *Pharm. Res.*, 2001, **18**, 662–666.
- 46 D. E. López, K. Suwannakarn, J. G. Goodwin and D. A. Bruce, *Ind. Eng. Chem. Res.*, 2008, **47**, 2221–2230.
- 47 Z. Zeng, J. Chen, L. Cui, W. Xue and Y. Che, *Recent developments on the mechanism and kinetics of esterification reaction promoted by various catalysts*, INTECH Open Access Publisher, 2012.
- 48 J. Lilja, D. Y. Murzin, T. Salmi, J. Aumo, P. Mäki-Arvela and M. Sundell, *J. Mol. Catal. A: Chem.*, 2002, **182–183**, 555–563.
- 49 V. K. S. Pappu, V. Kanyi, A. Santhanakrishnan, C. T. Lira and D. J. Miller, *Bioresour. Technol.*, 2013, **130**, 793–797.
- 50 Y. Liu, E. Lotero and J. G. Goodwin Jr., *J. Catal.*, 2006, **243**, 221–228.
- 51 M. Charton, *J. Am. Chem. Soc.*, 1975, **97**, 1552–1556.
- 52 H. Fujimoto, Y. Mizutani, J. Endo and Y. Jinbu, *J. Org. Chem.*, 1989, **54**, 2568–2573.
- 53 Y. Kuwahara, W. Kaburagi, K. Nemoto and T. Fujitani, *Appl. Catal., A*, 2014, **476**, 186–196.
- 54 D. R. Fernandes, A. S. Rocha, E. F. Mai, C. J. A. Mota and V. Teixeira da Silva, *Appl. Catal., A*, 2012, **425–426**, 199–204.
- 55 S. G. Newman and K. F. Jensen, *Green Chem.*, 2013, **15**, 1456–1472.
- 56 S. Furuta, H. Matsushashi and K. Arata, *Catal. Commun.*, 2004, **5**, 721–723.
- 57 S. Furuta, H. Matsushashi and K. Arata, *Appl. Catal., A*, 2004, **269**, 187–191.
- 58 K. Suwannakarn, E. Lotero, J. G. Goodwin Jr. and C. Lu, *J. Catal.*, 2008, **255**, 279–286.
- 59 M. G. Cutrufello, U. Diebold and R. D. Gonzalez, *Catal. Lett.*, 2005, **101**, 5–13.
- 60 D. Țărbușiu, J. Q. Li and S. Cameron, *Appl. Catal., A*, 1997, **154**, 173–184.

