

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

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Electronic Supporting Information

S1 Experimental

a) Catalyst characterization

Surface areas and pore sizes were measured by N₂ physisorption on a Quantasorb Nova 2000 and 4000 instruments, after sample outgassing at 120 °C for 2 h. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) method over the range $P/P_0 = 0.03–0.18$, where a linear relationship was maintained. Pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model applied to the desorption branch of the isotherm. Sulfur content of the materials was measured using a Thermo Scientific Flash 2000 organic elemental analyser calibrated to sulfanilamide, fitted with Cu/CuO CHNS quartz tube and a TCD. Samples were prepared by adding ~10 mg catalyst and ~2 mg V₂O₅ to tin crucibles. Propylamine adsorption/TGA-MS was performed by exposing the samples to propylamine overnight. Excess physisorbed propylamine was removed in *vacuo* at room temperature prior to temperature programmed desorption on a Mettler Toledo TGA/DSC 2 STAR^e System equipped with a Pfeiffer Vacuum ThermoStar™ GSD 301 T3 mass spectrometer.

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. Samples were outgassed for 2 h at 120 °C to remove physisorbed water and impurities on the surface prior to exposure to the alcohol pulses. Surface properties were determined according to literature methods.^{1, 2} The measurements were performed at infinite dilution in the Henry region ($p/p_0 = 0.04$) to exclude interactions between probe molecules on material surface. Approximately 5 mg of catalyst was packed into a glass column (300 mm × 2 mm i.d.) by tapping until no cracks or hollows were present in the powder bed. The columns were loosely stoppered with quartz wool in both ends. Then the powder filled columns were outgassed under helium for 2 h at 120 °C to remove adsorbed water and impurities on the surface. Probes including methanol, ethanol and 1-propanol were carried into the column by helium with a gas flow rate of 10 sccm (standard cubic centimeter per minute), and the retention times were detected by a flame ionization detector (FID). The dead volume, the retention volume if there is no interaction between probe and solid, was calculated based on the elution time of methane which was run at a concentration of 0.1 p/p_0 , where p is the partial pressure and p_0 is the saturation pressure. The heat of adsorption for each alcohol is calculated from the gradient of the plot of $\ln V/T$ and $1/T$.

b) Esterification reactions

Batch esterification was performed using a Radleys Carousel Reactor Station at atmospheric pressure. 150 mmol alcohol (methanol, ethanol, 1-propanol or 1-butanol), 5 mmol of propanoic (C₃), hexanoic (C₆), lauric (C₁₂) or palmitic (C₁₆) acid, and 0.5 mmol of dihexyl ether (as an internal standard) were added to a sealed glass reactor tube under stirring at 60 °C. Catalyst was subsequently introduced (25 mg Bulk SZ or 50 mg SZ/SBA-15), and aliquots of the reaction mixture periodically withdrawn and filtered and diluted with dichloromethane for analysis on a GC. C₃ and C₆ acid esterification was monitored using a Varian 450-GC equipped with a Phenomenex ZB-5HT Inferno 15 m × 0.32 mm × 0.10 μm while analysis of reaction products from lauric and palmitic acid esterification employed a 1079 programmable, direct on-column injector and Phenomenex ZB-1 HT Inferno 15 m × 0.53 mm × 0.15 μm capillary column. All catalytic profiles are an average of 3 injections per sample. Conversions reported are based upon change in the concentration of the organic acid, with initial rates calculated over the first hour of

reaction, wherein the conversion profile was linear. Turnover frequencies (TOF) were determined from the initial reaction rate which was normalised to the acid site loadings as determined from propylamine adsorption/TGA-MS.

Continuous flow esterification of propanoic acid and methanol was conducted using a commercial Uniqsis FlowSyn reactor. An integral HPLC pump delivered a liquid stream of methanol (150 mmol) and propanoic acid (5 mmol) to a packed bed microreactor, heated to 60 °C, at flow rates between 0.1 cm³.min⁻¹ to 1 cm³.min⁻¹. 65-75 mg catalyst was diluted with quartz beads (Sigma Aldrich, mesh size = 325) to minimise back pressure, and packed within a 10 mm i.d. x 100 mm OMNIFIT® glass column to give a total bed volume of 1.7 cm³, held in place between quartz wool plugs at either end of the column. The reactor was oriented vertically and the liquid stream fed in an up-flow direction to minimise settling and maximise permeation of the reaction mixture through the catalyst bed. Neither fluidisation nor compaction of the catalyst bed was observed under any conditions. The exit stream passed through a needle valve and backflow regulator prior to off-line sampling for GC analysis.

S2 Results and Discussion

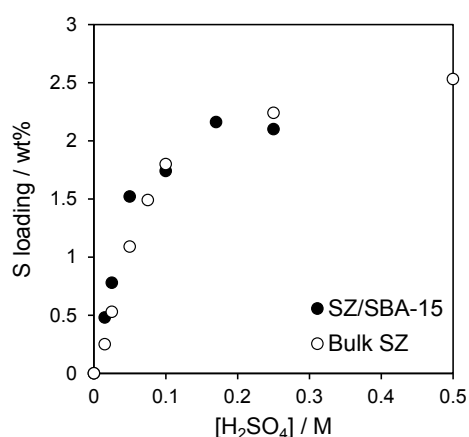


Figure S1. Bulk sulfur analysis from CHNS for SZ and SZ/SBA-15 series

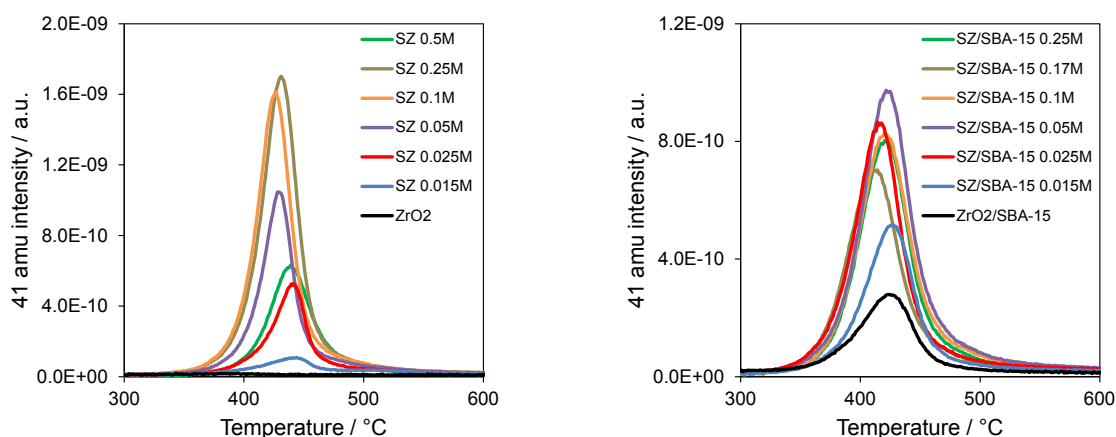


Figure S2. Propylamine TPD showing 41 amu mass spectrometer signal for reactively formed propene as a function of temperature for measuring acid site loading of left) SZ and right) SZ/SBA-15 catalysts.

N₂ porosimetry isotherms

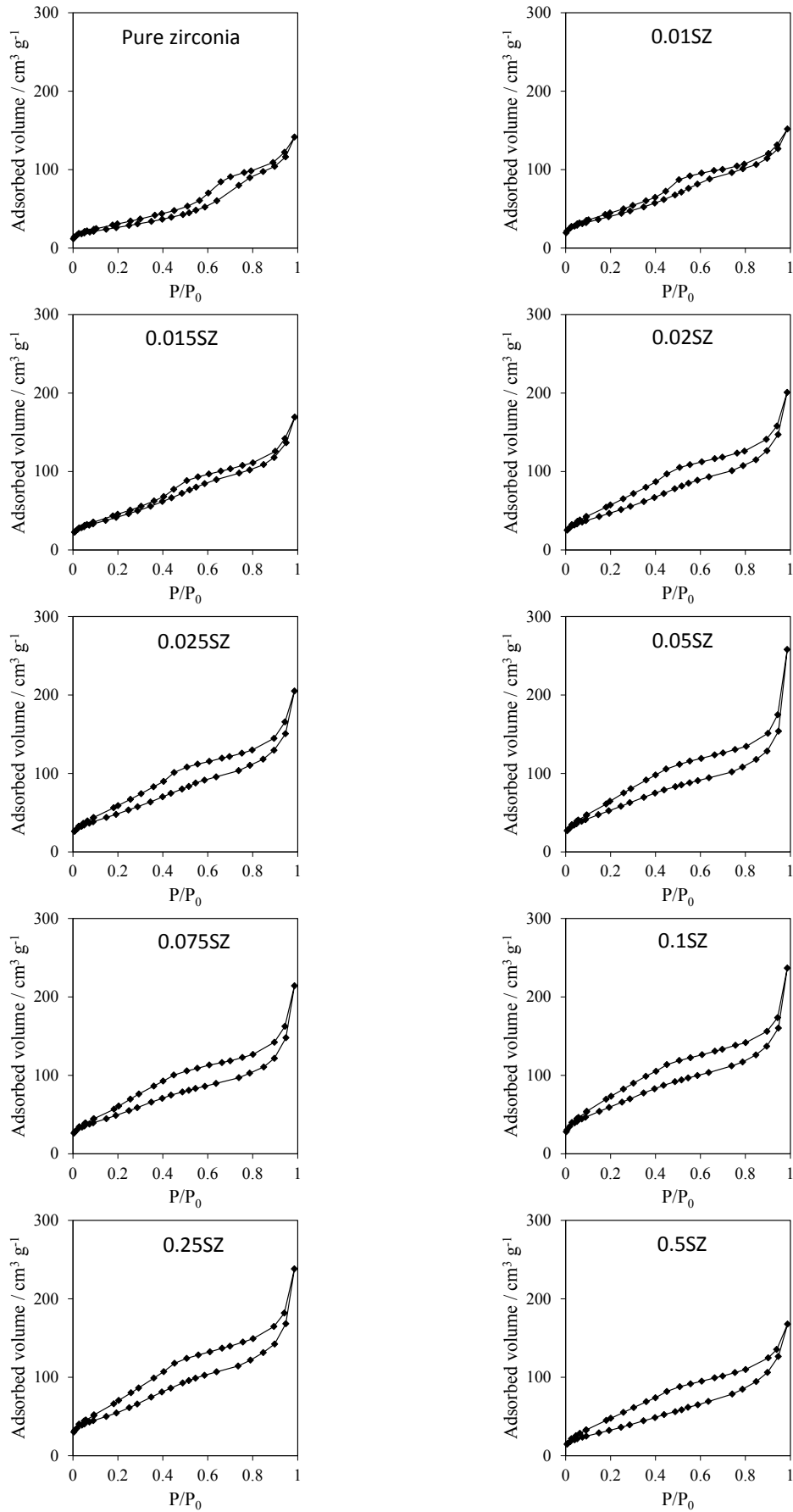


Figure S3. N₂ porosimetry isotherms for bulk SZ materials

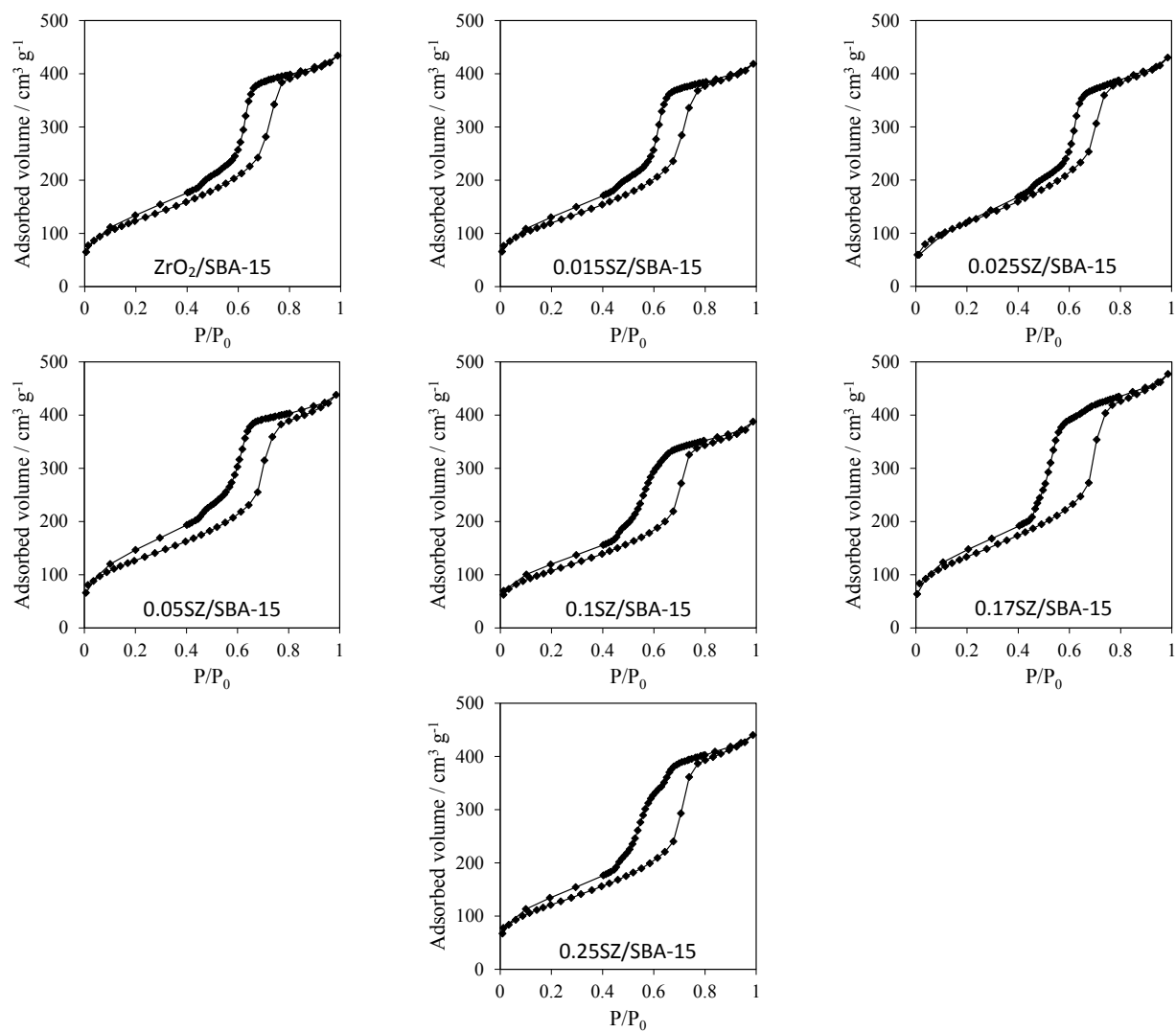


Figure S4. N₂ porosity isotherms for SZ/SBA-15 materials

Propanoic acid esterification - Effect of alcohol type

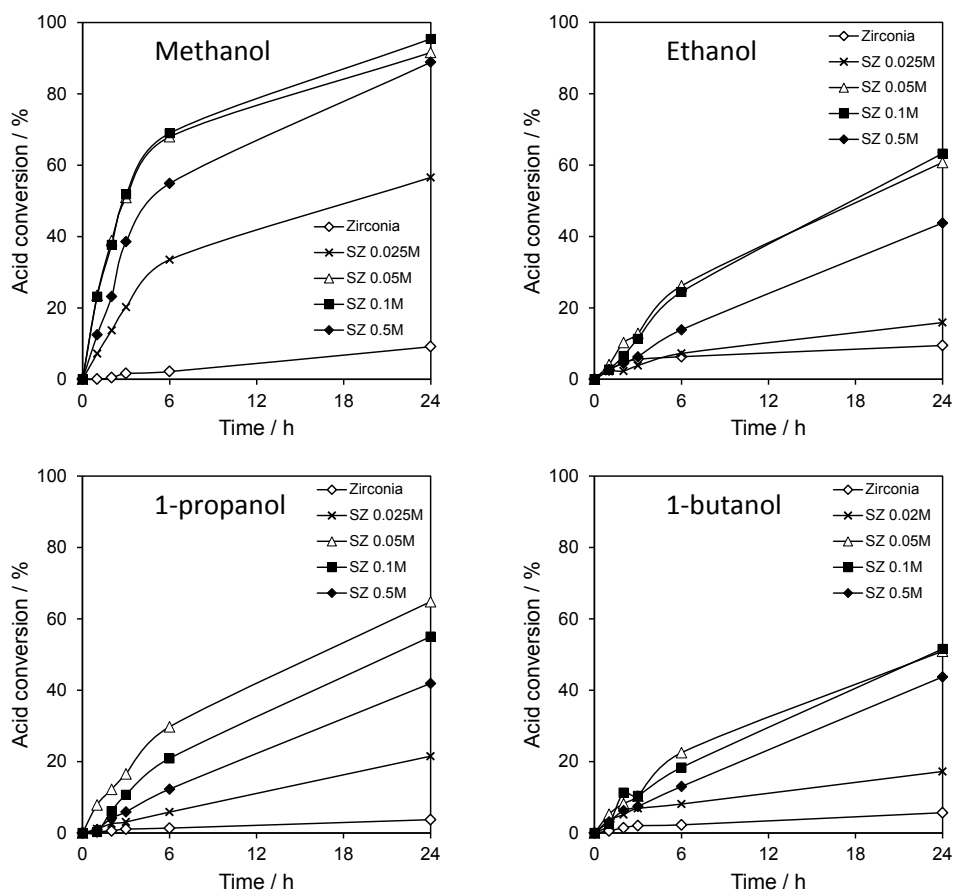


Figure S5. Reaction profiles of propanoic acid conversion with C_1-C_4 alcohols over SZ catalysts at 60°C as a function of SO_4 content

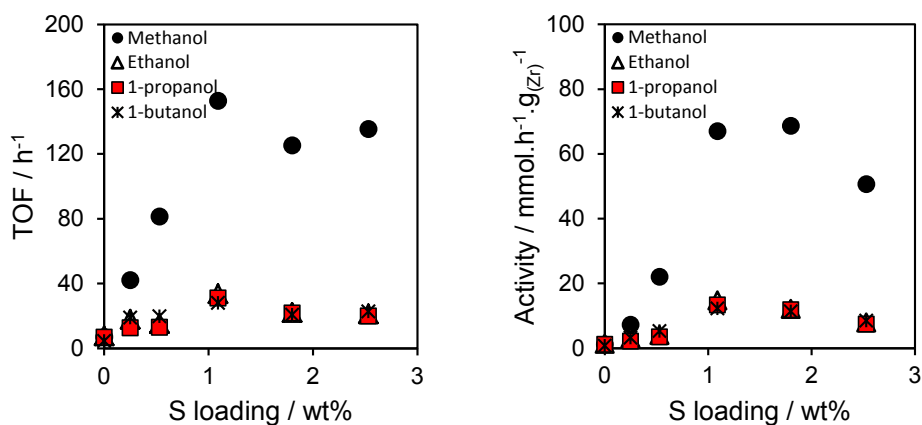


Figure S6. Left) TOFs and right) activity for esterification of propanoic acid with C_1-C_4 alcohols over bulk SZ as a function of SO_4 content.

Esterification with methanol over bulk SZ - Effect of carboxylic acid alkyl chain length

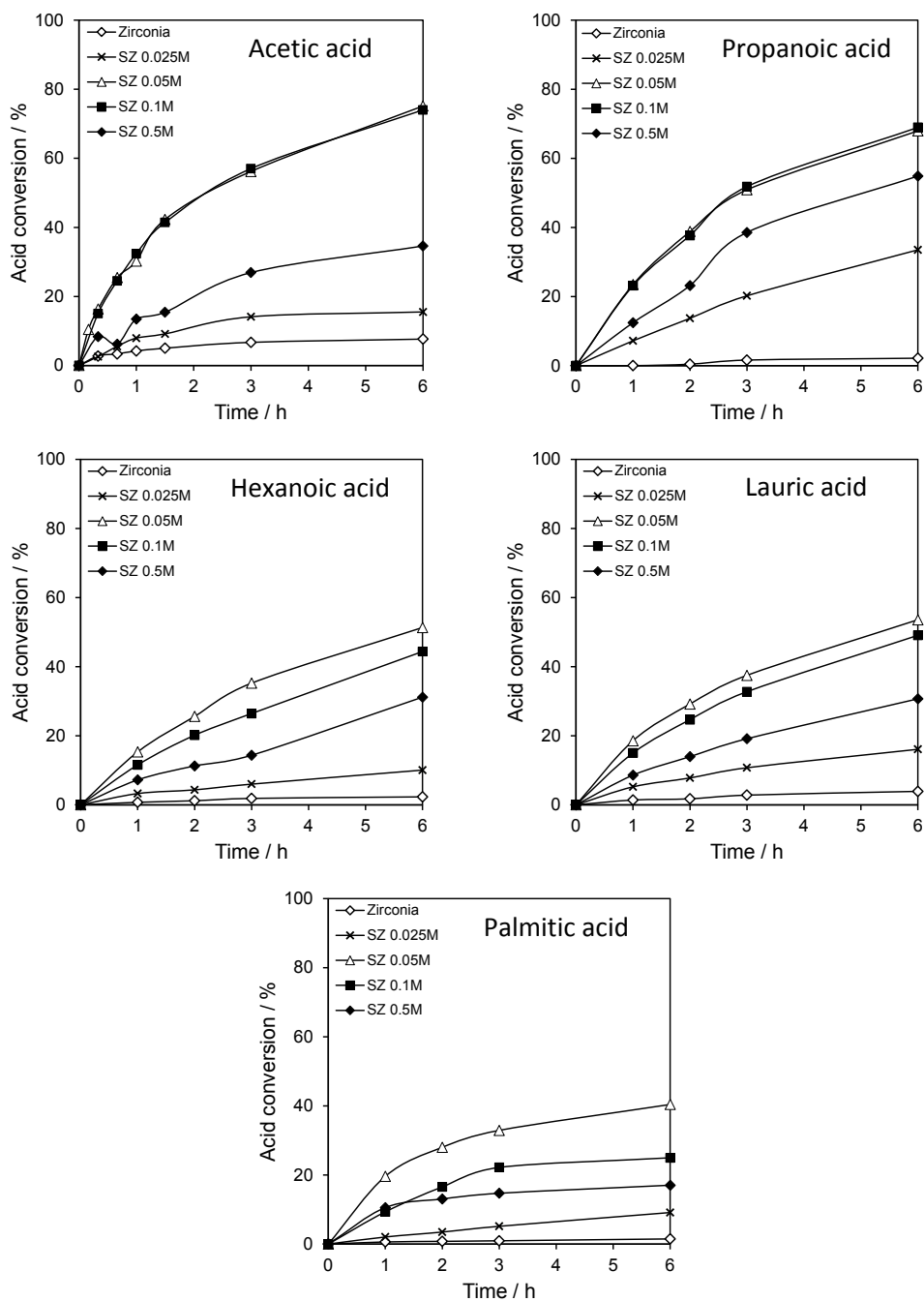


Figure S7. Reaction profiles for conversion of C₂-C₁₆ carboxylic acids in esterification with methanol over SZ catalysts at 60°C as a function of SO₄ content

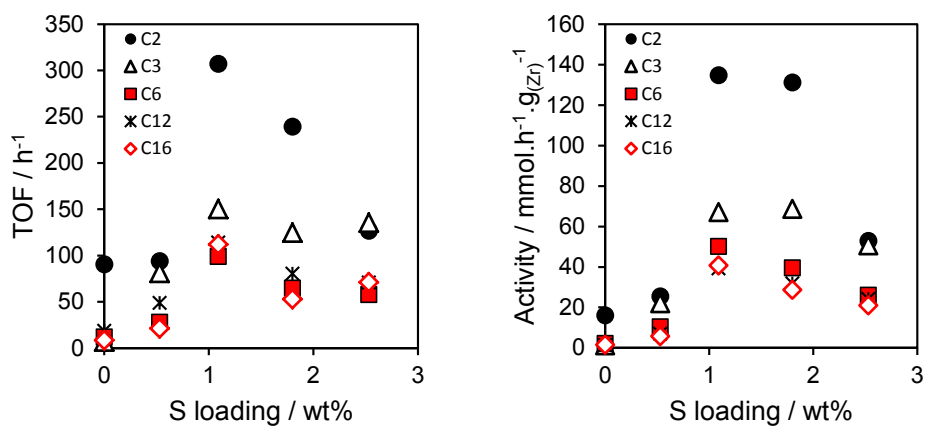


Figure S8. Left) TOFs and right) activity for esterification of C₂-C₁₆ carboxylic acids with methanol over bulk SZ as a function of sulfur loading.

Esterification with methanol over SZ/SBA-15 - Effect of carboxylic acid alkyl chain length

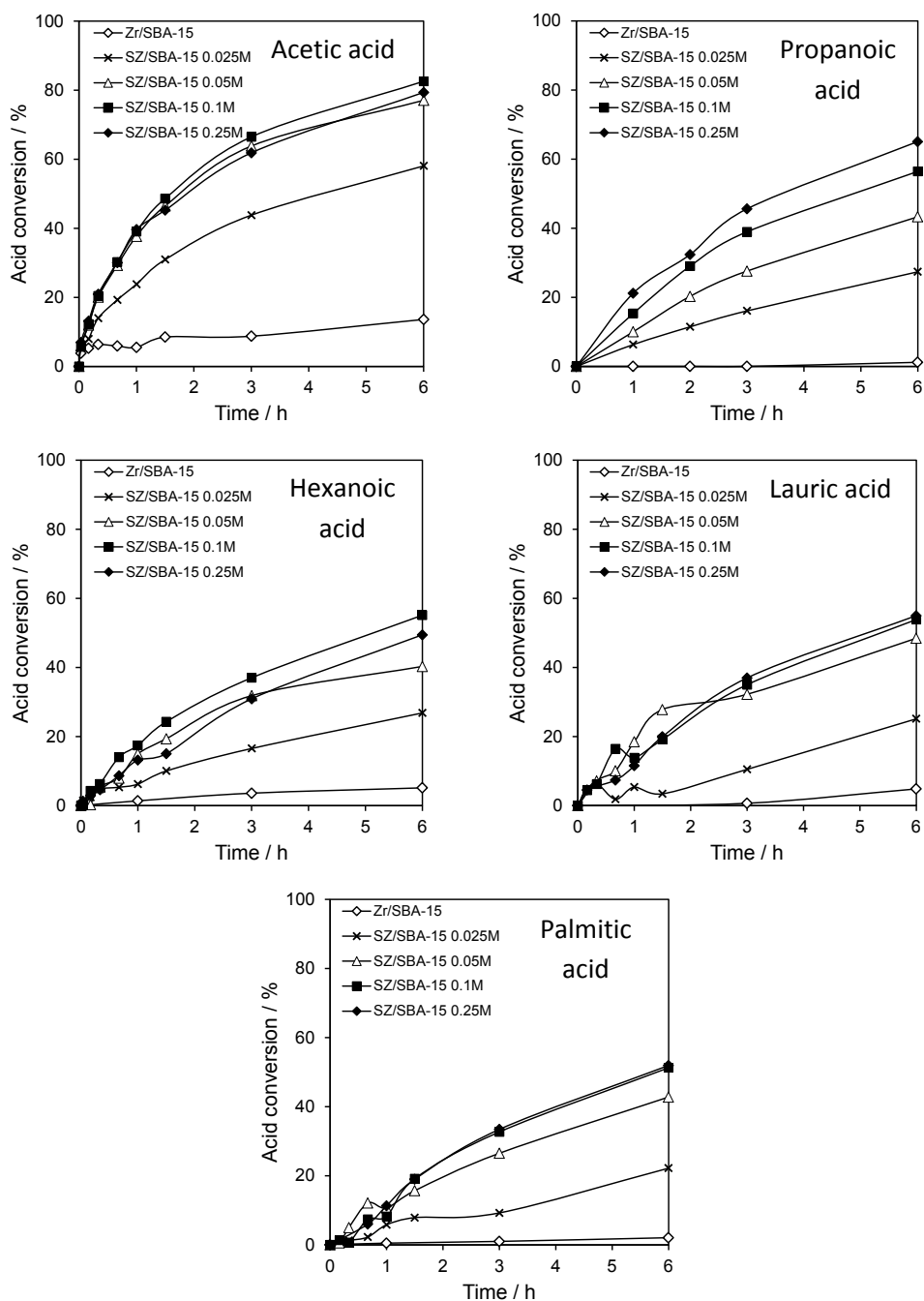


Figure S9. Reaction profiles for the conversion of C₂-C₁₆ carboxylic acids in esterification with methanol over SZ/SBA-15 catalysts at 60°C as a function of SO₄ content.

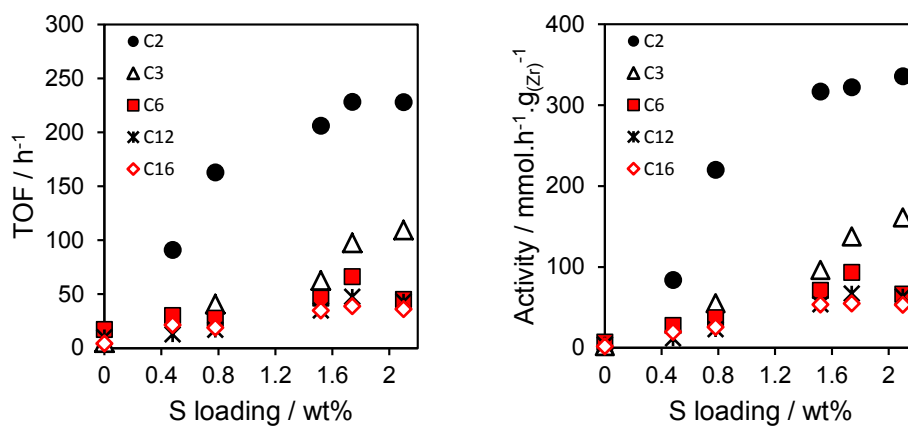


Figure S10. Left) TOFs and right) activities for esterification of C₂-C₁₆ carboxylic acids with methanol as a function of SZ/SBA-15 sulfur loading.

Calculation of rate constant

Pseudo first order kinetic analysis of the reaction profiles was possible due to the large excess of alcohol (acid:alcohol = 1:30 mol:mol). The kinetic rate equation is as shown below:

$$-r_A = k_1 C_A = k_2 C_{B0} C_A = k_3 C_{cat} C_{B0} C_A \quad (k_1 = k_2 C_{B0}), (k_2 = k_3 C_{cat}) \quad \text{Equation S1}$$

$$-\frac{dC_A}{dt} = \frac{C_{A0} dX_A}{dt} = k_1 C_{A0} (1 - X_A) \quad \text{Equation S2}$$

$$-\ln(1 - X_A) = k_1 t \quad \text{Equation S3}$$

Where C_A = concentration of acid (L mol^{-1}); C_{B0} = original concentration of the alcohol (L mol^{-1}); C_{cat} = catalyst loading in the reactant mixture (g L^{-1}); k_3 = actual rate constant for esterification ($\text{L}^2 \text{mol}^{-1} \text{s}^{-1} \text{g}_{cat}^{-1}$).

Table S1. Rate constants for the SZ catalysed esterification of propanoic acid with alcohols at 60°C

	k_1 s^{-1}	k_2 $\text{dm}^3 \cdot \text{s}^{-1} \text{mol}^{-1}$	k_3 $\text{dm}^6 \cdot \text{s}^{-1} \text{mol}^{-1} \text{g}_{cat}^{-1}$
Methanol	6.71E-05	2.91E-06	7.56E-07
Ethanol	1.44E-05	8.77E-07	3.20E-07
1-propanol	1.33E-05	1.03E-06	4.78E-07
1-butanol	1.11E-05	1.04E-06	5.88E-07

Table S2. Rate constants for the SZ catalysed esterification of carboxylic acids with methanol at 60°C

	k_1 s^{-1}	k_2 $\text{dm}^3 \cdot \text{s}^{-1} \text{mol}^{-1}$	k_3 $\text{lit}^2 \text{s}^{-1} \text{mol}^{-1} \text{g}_{cat}^{-1}$
Acetic acid	1.30E-04	5.53E-06	1.41E-06
Propanoic acid	6.71E-05	2.91E-06	7.56E-07
Hexanoic acid	4.21E-05	1.89E-06	5.08E-07
Lauric acid	4.56E-05	2.16E-06	6.12E-07
Palmitic acid	4.86E-05	2.46E-06	7.50E-07

Taft plots

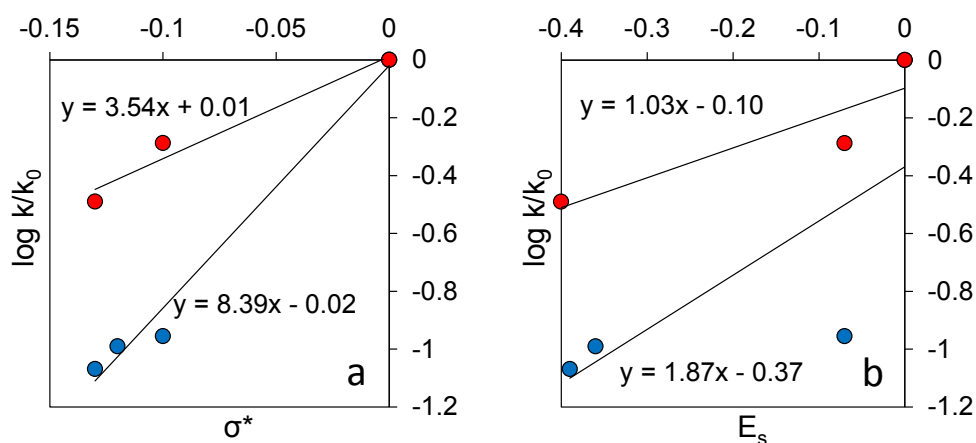


Figure S11. Taft relationship for increased alkyl chain lengths in (●) alcohols and (●) carboxylic acids

$$\log\left(\frac{k_s}{k_{CH_3}}\right) = \rho^* \sigma^* + \delta E_s$$

Equation S4. Taft equation

Table S3. Polar (σ^*) and steric (E_s) substituent constants for aliphatic substituents

Substituent	Polar substituent constant (σ^*) ³	Steric substituent constant (E_s) ⁴
H	+0.49	+1.24
CH ₃	0	0.00
C ₂ H ₅	-0.1	-0.07
Cyclo-C ₄ H ₇	-	-0.06
ClCH ₂	-	-0.19
<i>n</i> -C ₃ H ₇	-0.12	-0.36
<i>n</i> -C ₄ H ₉	-0.13	-0.39
<i>n</i> -C ₅ H ₁₁	-	-0.40
<i>i</i> -C ₅ H ₁₁	-	-0.35
<i>n</i> -C ₈ H ₁₇	-	-0.33
<i>i</i> -C ₄ H ₉ CH ₂ CH ₂	-	-0.34
C ₆ H ₅ CH ₂	-	-0.38
C ₆ H ₅ CH ₂ CH ₂	-	-0.43
C ₆ H ₅ CH ₂ CH ₂ CH ₂	-	-0.45
<i>i</i> -C ₃ H ₇	-0.19	-0.47
Cyclo-C ₅ H ₉	-	-0.51
Cyclo-C ₆ H ₁₁	-	-0.79
<i>i</i> -C ₄ H ₉	-	-0.93
Cyclo-C ₆ H ₁₁ CH ₂	-	-0.98
(CH ₃)(C ₂ H ₅)CH ₂	-	-1.13

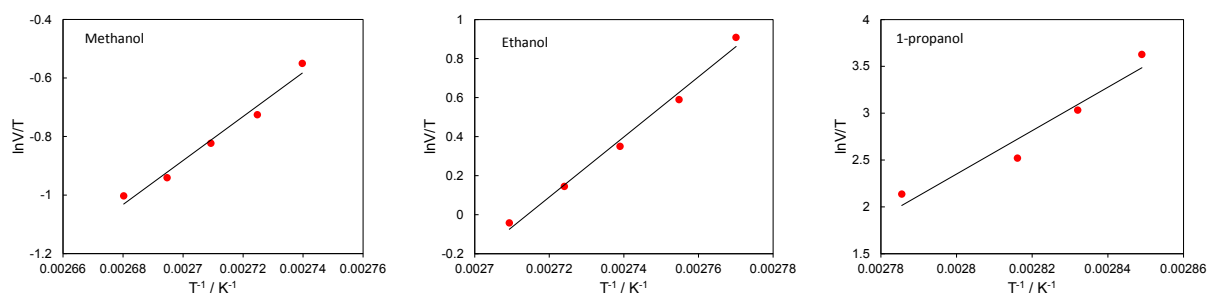


Figure S12. Heat of adsorption plots for methanol, ethanol and 1-propanol over 0.05SZ at infinite dilution

Esterification of oleic, linoleic and levulinic acid with methanol

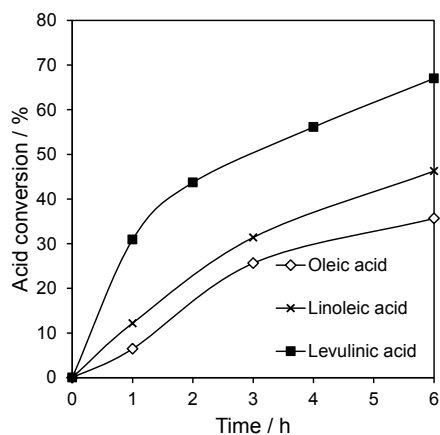


Figure S13. Reaction profile for esterification of oleic, linoleic and levulinic acid with methanol over 0.05SZ at 60°C.

Reference

1. M. C. Gutierrez, J. Rubio, F. Rubio and J. L. Oteo, *Journal of Chromatography A*, 1999, **845**, 53-66.
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4. R. W. Taft, *Journal of the American Chemical Society*, 1952, **74**, 3120-3128.