Supporting information for the article

Sulfated zirconia as a robust super acid catalyst for multiproduct fatty acid esterification

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Synthesis of the catalysts

Table S1. Synthesis condition for chlorosulfated zirconia catalysts

Entry	Catalyst	Sulfonation agent	Drying $Zr(OH)_4$
1	SSZr	15 ml sol. H_2SO_4 0.87 M / g $Zr(OH)_4$: 0.013 mol H_2SO4 / g $Zr(OH)_4$	64 h
2	ClSZr-1	15 ml sol. $HClSO_3$ 0.87 M / g $Zr(OH)_4$: 0.013 mol $HClSO_3$ / g $Zr(OH)_4$	64 h
3	ClSZr-2	15 ml sol. $HClSO_3$ 0.87 M / g $Zr(OH)_4$: 0.013 mol $HClSO_3$ / g $Zr(OH)_4$	16 h
4	ClSZr-3	50 ml sol. $HClSO_3$ 0.5 M / g $Zr(OH)_4$:	16 h

Porosity studies

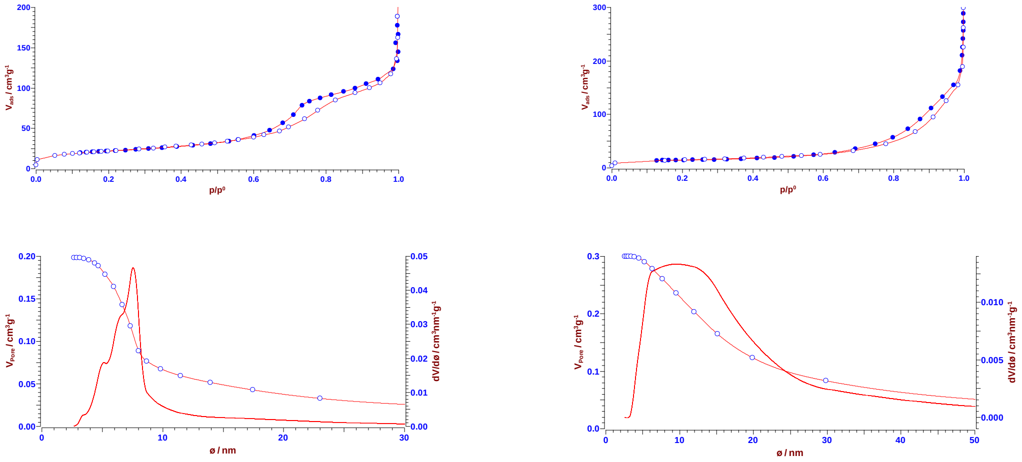

Figure S1 The nitrogen adsorption isotherms and the pore distribution for sulfated SSZr-1(left) and chlorsulfated ClSZr-1 (right) catalysts.

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Temperature Programmed Desorption

A measure of the acid site strength is obtained from the total acidity measured by temperature programmed desorption (TPD) analysis. We see that in the SSZr-1(UVS2) catalyst most of the acid sites are located at low temperatures (150–220 °C) as well as around 400 °C. In contrast, for the ClSZr-1(UVC 4) catalyst there is a large peak at higher temperature, namely around 530–540 °C. Note that acid sites located above 400 °C are considered as “super-acidic”.

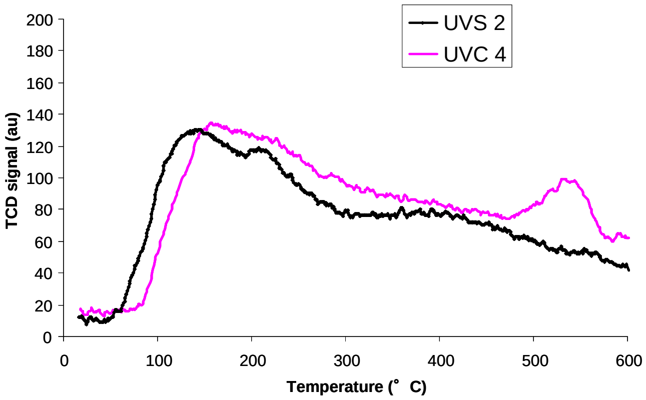

Figure S2 TPD analysis with ammonia for total acidic sites characterization.

Table S2 Effect of sulfur level on sulfated zirconia catalysts calcined at 650 °C.

Catalyst	Sulfur (%)	Surface Area (m^2/g)	Total acidity (μmol/g)
SSZr-1	3.2	78	134
ClSZr-1	7.2	52	195

Additional esterification curves

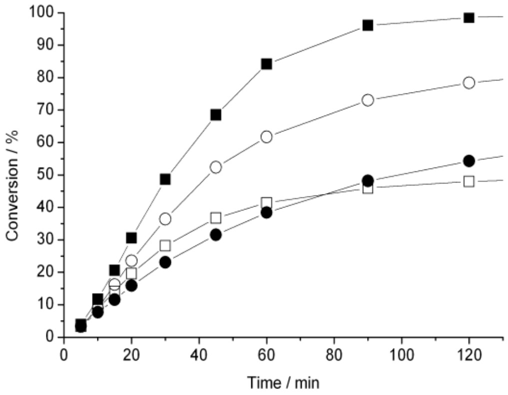

Figure S3 Esterification of lauric acid with 2-ethylhexanol at 140 °C using various acid:alcohol molar ratios: 1:2 (■),1:1 (○), 2:1 (□). The catalyst concentration is 2% w/w catalyst/acid, allowing a better visualization of the influence of alcohol concentration on the initial part of the reaction profiles. For comparison, the thermal background reaction for a 1: 1 ratio without any catalyst is also shown (●).

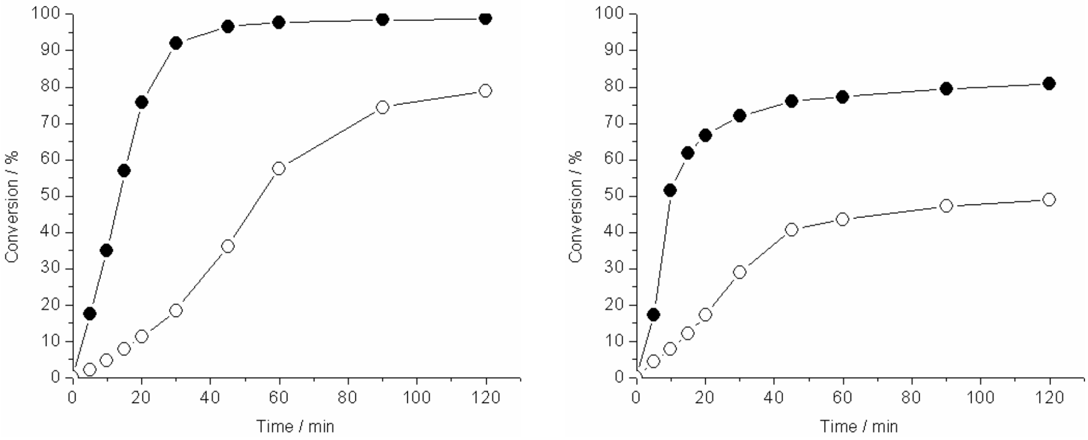

Figure S4 Comparing the kinetic behavior of lauric acid esterification with *n*-propanol (●) and *iso*-propanol (○) at different mole ratios, Reaction conditions: acid:alcohol molar ratio of 1:1 (right) and 1:3 (left); 5 wt % catalyst, temperature 133 °C.

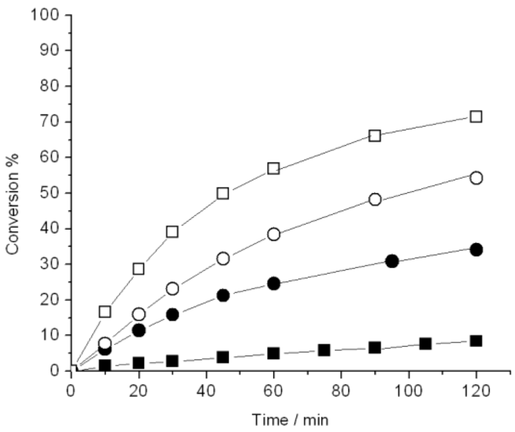

Figure S5 Comparing the background reaction (thermal reaction in the absence of any catalyst) of lauric acid esterification with various alcohols at different temperatures. Reaction conditions: acid:alcohol 1:1, 170 °C (*iso*-propanol ●), 140 °C (2-ethylhexanol ,○), 160 °C (2-ethylhexanol, ☐); 95 °C (*n*-propanol, acid: alcohol mole ratio of 1:5, ■).

Catalyst leaching experiments

The leaching of sulphonic groups was tested by filtering and re-adding the solid catalyst. In the first experiment the catalyst was present throughout the reaction. In the second the catalyst was filtered off after 30 min, and then re-added 45 min later. Comparing the two reactions showed that no appreciable leaching of active acid groups occurs.

Deriving the kinetic equations for fatty acid esterification

Considering the results shown in Figures 5–7 in the main manuscript as well as Figure S3, we propose a set of kinetic equations for preliminary design purposes. The differential equation describing the conversion-time dependency in a batch reactor is

$$c_{A0}\frac{dX_A}{dt} = k_f[W]c_{A0}^2[(1-X_A)(M-X_A)-X_A^2/K_c] \qquad \text{(S1)}$$

In the above equation, X_A is the conversion of the reference reactant (here the fatty acid) with the initial molar concentration c_{A0}, W the amount of catalyst as %weight with respect to fatty acid amount, $M = c_{B0}/c_{A0}$ the initial molar ratio of reactants, while K_c the equilibrium constant based on concentrations. If K_c is assumed or known from independent equilibrium measurements, the forward kinetic constant k_f can be obtained by simple linear regression from the following equation:

$$k_f[W]c_{A0}t(1-1/K_c)(X_1-X_2) = \ln\frac{X_2(X_1-X)}{X_1(X_2-X)} \qquad \text{(S2)}$$

where X_1 and X_2 are the roots of chemical equilibrium equation:

$$(1-1/K_c)X^2-(M+1)X+M=0 \qquad \text{(S3)}$$

respectively,

$$\begin{aligned} X_1 &= X_{eq} = (M+1) - a_2/2a_1 \\ X_2 &= (M+1) + a_2/2a_1 \end{aligned} \tag{S4}$$

in which

$$\begin{aligned} a_1 &= 1 - 1/K_{eq} \\ a_2 &= \sqrt{(M+1)^2 - 4a_1 M} \end{aligned} \tag{S5}$$

Note also that the initial concentration of the reference reactant depends on the initial molar ratio of reactants. Assuming additive volumes gives:

$$c_{A0} = 1/\left(\frac{M_A}{\rho_A} + M\frac{M_B}{\rho_B}\right) \tag{S6}$$

with (M_A, M_B) and (ρ_A, ρ_B) the molecular weights and the densities of the reactants. The densities (g/l) of lauric acid, NPA and IPA are 0.809, 0.693 and 0.660 at 133 °C and 0.796, 0.672 and 0.635 at 150 °C as calculated by the simulation package Aspen Plus^{TM}. For the molar ratios 1, 3, and 5 the initial molar concentration of the fatty acid are 2.918, 1.920 and 1.422 using IPA and 2.920, 1.923 and 1.437 using NPA.

X-ray diffraction of sulfated zirconia

The formation of crystalline sulfated zirconia via de impregnation process was studied by powder X-ray diffraction. The non-calcined ZrO_2 precursor contains only one broad peak centred at *ca.* 30°. This indicates an amorphous character of the material. The XRD of ZrO_2 shows the presence of both monoclinic and tetragonal phases. Generally, pure zirconia transforms into a monoclinic phase (M) from a tetragonal phase (T) above the calcination temperature of 400 °C. However, this transformation is retarded in sulfated zirconia. Figure S6 indicates that the monoclinic phase is the predominant one for catalyst ClSZr-1. This indicates that the impregnated sulfate ions affect the phase modification of zirconia.

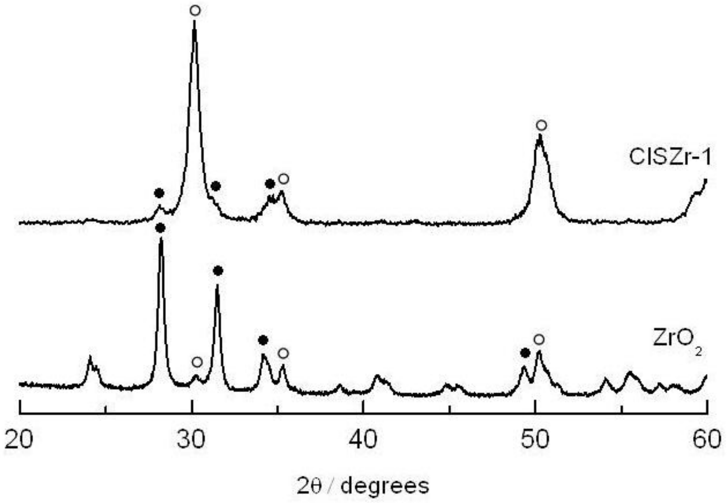

Figure S6: X-ray powder diffraction patterns of pure and cholorosulfonate-promoted zirconia samples calcined at 650 °C. The '○' and '●' symbols denote the characteristic lines of tetragonal and monoclinic zirconia, respectively.

Thermogravimetric analysis of sulfated zirconia

For both catalysts SSZr-1 and ClSZr dehydration occurs up to 200 °C. Above 600 °C, the mass loss can be correlated with the decomposition of surface sulfate ions.

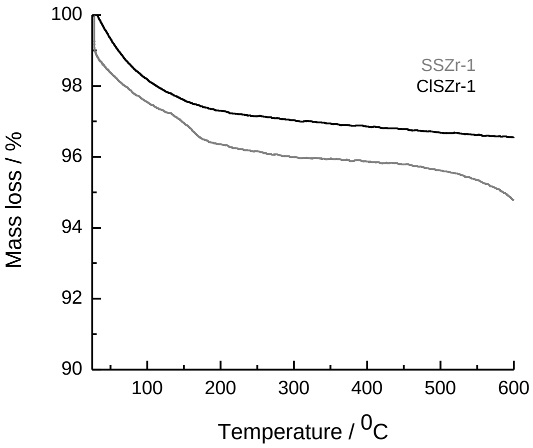

Figure S7: The TGA curves of SSZr-1 and ClSZr-1 catalysts calcined at 650 °C.