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Self-assembled sulfated zirconia nanocrystals with mesoscopic void space synthesized via ionic liquid as a porogen and its catalytic activity for the synthesis of biodiesels

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Department of Material Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata - 700032, India \*Corresponding author. Tel.: +91 33 2473 4971, E-mail: msab@iacs.res.in Graphical abstract

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Self-assembled  $ZrO_2$  nanocrystals have been synthesized through a facile steam-assisted ionothermal method using 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) as a porogen. The sulphonated,  $ZrO_2$  has been employed as efficient, recyclable and environmentally benign heterogeneous catalyst for the synthesis of biodiesel products.

#### Highlights

First synthesis of self-assembled ZrO<sub>2</sub> nanocrystals by using an ionic liquid as porogen. Steam-assisted ionothermal method followed by sulphonation to yield sulphated zirconia. An easy protocol for designing mesoporosity and tiny crystalliates of sulphated zirconia nanoparticles.

Sulfated zicronia material showed high catalytic activity for the synthesis of biodiesel products based on long chain fatty acids.

#### Abstract

Self-assembled ZrO<sub>2</sub> nanocrystals have been synthesized through a facile chemical route via steam-assisted ionothermal method using 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) as a porogen. The template-free material has been sulphonated by 1(N) H<sub>2</sub>SO<sub>4</sub> at room temperature followed by calcination in air at 723 K. Both ZrO<sub>2</sub> and the sulfonated zirconia materials are thoroughly characterized by powder X-ray diffraction (PXRD), ultra high-resolution transmission electron microscopy (UHR-TEM), Fourier Transform Infrared spectroscopy (FT IR), FE-SEM, N<sub>2</sub> sorption and NH<sub>3</sub>-TPD analyses. The sulfonated material has been employed as efficient and environmentally benign heterogeneous catalyst for the synthesis of biodiesels based on long chain fatty acid esters. The catalyst can be easily recovered and reused at least for five times without significant decrease in its catalytic activity.

**Keywords**: Sulphated zirconia nanocrystals; ionic liquid; heterogeneous catalyst; long chain fatty acids; biodiesel.

#### Introduction

Template directed synthesis of metal oxide nanostructures with nanoscale porosity and crystallinity is of great interest across several interdisciplinary fields of research due to their widespread potential applications [1]. Conventional sol-gel process produced a large library of mesoporous metal oxides over last decade but there are some major drawbacks in their synthesis. Resulting materials are usually amorphous in nature and owing to the involvement of high temperature calcination process often there is collapse in resulting mesotructure [2-6]. Various research groups have reported synthesis of mesoporous  $ZrO_2$ nanoparticles using templating pathways using CTAB [7], nano-propping using gemini surfactants [8], Pluronic P123 and Brij56 [ $C_{16}(EO)_{10}$ ] [9] as structure directing agents or via non-templating pathway [10]. Ward et al. have reported synthesis of mesoporous silica embedded with nanocrystalline sulfated zirconia material using ionic liquid as a template [11]. On the other hand, ionic liquids due to their highly charged structure can act as a good capping agent to stabilize the tiny nanoparticles and thus ionothermal synthesis for designing microporous and mesoporous materials is gaining increasing interest [12]. Moreover, varying the alkyl chain length of the ionic liquid molecules can direct the surface molecularly

imprinted polymers [13]. Upon removal of these ionic liquid molecules trapped inside the cages of the nanoparticles via calcination, nanoscale void space could be generated and thus the ionic liquid can act as structure directing agent for the synthesis of porous metal oxides. We have recently synthesized few-nanometer-sized cuboid-shaped  $TiO_2$  nanocrystals with exposed {001} facets by a novel stream-assisted ionothermal method [14]. It has been shown that ionic liquid can precisely control the shape of the materials, and thus they are chosen as the porogen in designing porous nanostructures. The choice of ionic liquid as mesopore directing is very demanding as they are environment friendly solvent because of their unique properties such as extremely low volatility, wide liquid temperature range, thermal stability, high ability of dissolving, excellent microwave absorbing ability, designable structures, high ionic conductivity etc. However, the synthesis of crystalline porous self-assembled  $ZrO_2$  nanocrystals with controllable pore structures with the aid of a template as a porogen is still a big challenge.

Today these nanocrystalline mesoporous oxides are employed largely for the development of sustainable energy and environmental clean-up [15,16]. From past decades fossil fuel reserve on the Earth is declining day by day due to the ever growing increase for the demand in fuels [17]. The scientists have come up with many alternative resources to continue the supply of energy and protect the nature from pollution mainly caused due to the burning of fossil fuels [18]. In this context biodiesel is made from renewable resources and low-cost feed stocks, containing a high concentration free fatty acids namely yellow greases, rendered animal fats, and trap greases [19]. Trivial method of biodiesel production primarily involves the esterification of free fatty acids or the transesterification of triglycerides with methanol or other short chain alcohols in the presence of acid or base catalysts [20]. In the case of industrial biodiesel production, which is mainly based on homogeneous base catalysis is associated with high production cost because of the involvements of neutralization and separation problems in the process. Apart from the increased production cost this procedure

suffers from several other limitations. For example, the free fatty acid content in the feedstock should be lower than 0.5 wt %, otherwise, biodiesel production will be badly hampered because of competitive reaction namely soap formation [21]. Use of concentrated sulphuric acid as a catalyst in the esterification reaction is an alternative way [22] but it is basically a homogeneous process, which is again corrosive and critical for waste separation [23]. For this reason solid acid catalysts are considered as suitable candidate to overcome these limitations of homogeneous catalysts. Heterogeneous catalysis based on solid acids has no corrosion issues and this process offers the certain advantages namely easy product separation by mere filtration and catalyst reusability [24]. Several solid acids are often extensively employed as heterogeneous catalyst for biodiesel production. Representative examples are zeolites [25,26], sulfonated carbonized sugar [27], organosulfonic acid functionalized mesoporous silica [28] sulfated ZrO<sub>2</sub> [29] sulfated-silica-ZrO<sub>2</sub> [30], SnO<sub>2</sub> based solid acid [31], porous organic-inorganic hybrid tin(IV) phosphonate [32], Zr-PMOs [33], ion exchange resins [34], mixed oxides [35], zirconium phosphate [36], organicinorganic hybrid porous aerogels [37] etc. Thus, it is highly desirable to develop a strong solid acid catalyst for this purpose, which could satisfy the following conditions. Firstly the catalyst should be highly dispersed in order to bring out a large number of active acid sites at its surface. Secondly, mesoporosity in the catalyst would be an added advantage because of the fact that it would be able to accommodate the relatively bulky fatty acids molecules. Finally, the catalyst needs to be water resistant or hydrophobic, since water is a common byproduct of the esterification process [30].

Herein, we wish to report the synthesis of the nanoscale assembly of nearly monodispersed, mesoporous and crystalline  $ZrO_2$  nanoparticles by using 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) as a porogen. Further, with the aid of sulfonation using 1(N) H<sub>2</sub>SO<sub>4</sub> followed by calcination at 723 K sulfonated mesoporous zirconia material is obtained. This sulfonated  $ZrO_2$  material has been employed as a heterogeneous catalyst for

the esterifiaction of long chain fatty acids at moderately low temperature (333 K). The present method is highly advantageous due to the fact that steam assisted ionothermal synthesis imparts high crystallinity along with the mesoporosity at the surface of the sulfonated  $ZrO_2$  material.

#### **Experimental Section**

#### Materials

1-butyl-3-methylimidazolium chloride ([bmim][Cl]) was purchased from Simplepharms Co., Ltd., China. Zirconium source zirconium (IV) butoxide solution (80 wt. % in 1-butanol) was purchased from Sigma-Aldrich. Concentrated sulphuric acid and methanol were purchased from E-Merck. Different long chain fatty acids were procured from Loba Chemie, India. For lauric, palmitic, stearic, sebacic and myristic acids the purity was 98-99% while for oleic acid it was 65-88%.

#### Synthesis of ZrO<sub>2</sub> nanocrystals M-IL-ZO-1:

Templated  $ZrO_2$  nanomaterial was synthesized by the following experimental procedure. First, 3.5 g of 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) was taken in a round bottom flask. It was then kept at 343 K in an oil bath for about 30 min under vigorous stirring. Then 3.84 g of zirconium (IV) butoxide solution was added slowly in the above mentioned pre-heated ionic liquid solution. The resulting mixture was stirred again for another 1 h at 343 K. Then, the mixture was transferred in a small Borosil glass vial and kept at room temperature for 24 h for aging. During this aging process gel formation occurred. The glass vial was then kept very carefully inside a Teflon container containing a 3 ml of water. Here  $ZrO_2$  gel in ionic liquid was separated from water by glass contact. The Teflon was then put in a stainless steel autoclave. Then the entire system was kept at 443 K for 24 h. This chemical approach is named as steam assisted ionothermal process. After this heat treatment the material was filtered, washed by plenty

of water and dried under vacuum. The as-synthesized solid was designated as M-IL-ZO-

1.

#### Synthesis of mesoporous sulphated ZrO<sub>2</sub> nanocrystals M-IL-SZO-1C:

Mesoporous sulphated zirconia was synthesized by treating 1 g of M-IL-ZO-1C in 15 ml 1(N) sulphuric acid at room temperature for 3 h. Then this was filtered, vacuum dried and calcined in the presence of air at 723 K for 4 h. The sulfonation process was repeated once more and the resulting material was designated as M-IL-SZO-1C.



Scheme 1. Schematic diagram showing mesoporous sulphated ZrO<sub>2</sub> nanocrystals M-IL-SZO-1C.

#### Esterifiaction of long chain fatty acids and trasesterification reactions

For each of the catalytic reaction 1 mmol of the reactant fatty acid was dissolved in 0.96 g methanol taken in a 50 ml round bottom flask. Then 80 mg of M-IL-SZO-1C catalyst was added into the RB flask. The reaction mixture was refluxed at 333 K for 8 h under the

nitrogen atmosphere. To study the progress of the reaction, the reaction mixtures were collected at different time intervals and the progress of the reactions were monitored by TLC.

#### **Characterization techniques**

Powder X-ray diffraction (XRD) patterns of different samples were taken in a Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu K $\alpha$  ( $\lambda$ =0.15406 nm) radiation. A JEOL JEM 6700 field emission scanning electron microscope (FE-SEM) was used for the determination of morphology of the resulting mesoporous oxide and sulfonated oxide materials. Ultra high resolution transmission electron microscopy (UHR-TEM) images of the mesoporous oxides were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. FT-IR spectra were obtained from a Nicolet Perkin-Elmer Spectrum 100 spectrophotometer. N<sub>2</sub> sorption studies of the materials were performed with the aid of Autosorb 1C surface area analyzer provided by Quantachrome, USA. Samples were degassed for 3 h at 423 K under high vacuum before analysis and all the analysis were performed in liquid N<sub>2</sub> temperature (77 K). NMR spectra (<sup>1</sup>H and <sup>13</sup>C NMR) of the biodiesel products were recorded using a Bruker DPX-400 NMR spectrometer using CDCl<sub>3</sub> as a solvent and TMS as an internal standard. NH<sub>3</sub>-TPD was performed using a Micromeritics Chemisorb 2720 equipped with a thermal conductivity detector. In a typical experiment for the TPD analysis M-IL-SZO-1C material was placed in a quartz cell at temperature 573 K under continuous 30 ml STP min<sup>-1</sup> flow rate of He for about 3 h followed by cooling to ambient temperature. It was then saturated by NH<sub>3</sub> gas at a flow rate of 30 ml STP min<sup>-1</sup> for about 30 min. Then the physically adsorbed NH<sub>3</sub> was removed by He gas flow. TPD experiment was then performed by raising the temperature with ramp of 5°C/min. The results were calculated by comparing with the standard TPD calibration curve.

#### **Results and Discussion**

Nanostructures of the sulfated zirconia nanoparticles:

The wide angle X-ray powder diffraction patterns of M-IL-ZO-1 and M-IL-SZO-1C materials are shown in Figure 1 (a and b, respectively). The XRD pattern reveals that both the M-IL-ZO-1 as well as M-IL-SZO-1C materials are showing tetragonal crystal phase for the  $ZrO_2$  nanopartiles. The broad diffraction peaks at 20 values of 30.30°, 35.03°, 50.54°, 60.16° and  $63.31^{\circ}$  can be indexed to the diffraction planes of (111), (200), (220), (311) and (222) planes of tetragonal phase of ZrO<sub>2</sub> [38-40], respectively. To further prove the absence of monoclinic phase we have calcined the material as high as 823 K and provided the PXRD pattern of that sample in Figure S2 (supporting information). This PXRD pattern can also be indexed as a mixture of monoclinic and tetragonal phases of ZrO<sub>2</sub>. Thus the monoclinic phase formation occurred at higher temperature. In order to calculate average particle size we have used Debye-Scherrer equation in the crystallite size calculation:  $D = 0.9\lambda/\beta \cos\theta$ , where D is the average crystallite size (nm),  $\lambda$  is the X-ray wavelength (Cu K $\alpha$  = 0.15406 nm),  $\beta$  is the full width at half maximum (FWHM) in radians and  $\theta$  is the Bragg diffraction angle of the most intense peak (here 111). Using this equation average crystallite size has been estimated for both M-IL-ZO-1 and M-IL-SZO-1C samples. For M-IL-ZO-1 and M-IL-SZO-1C the average crystallite size are 3.77 and 3.2 nm, respectively [41] which agrees very well with the HR-TEM results (see below).

#### **Framework and bonding:**

In Figure 2 FT-IR spectra of the M-IL-ZO-1 and M-IL-SZO-1C materials are shown. These spectra clearly showed the change of the IR bands due to sulfonation followed by calcinations of the materials. It is evident that there are additional peaks in the spectra of M-IL-SZO-1C compared to M-IL-ZO-1 material. The region v=1400 to 900 cm<sup>-1</sup> was very important for characterizing the present material due to the fact that presence of sulphate moieties can be inferred from this spectral region. Peak at 1220 cm<sup>-1</sup>, 1130 cm<sup>-1</sup>, 1047 cm<sup>-1</sup> confirms the presence of sulphate group bound to ZrO<sub>2</sub> nanocrystals because these are S-O asymmetric stretching frequencies. These peaks are absent in M-IL-ZO-1 material. The band

at 1624 cm<sup>-1</sup> can be indexed as deformation vibration mode of bounded water molecules at the catalyst surface [42].

#### **Electron microscopic analyses:**

In Figure 3 the FE-SEM images of the M-IL-ZO-1 and M-IL-SZO-1C are shown. The images revealed that both the materials are composed of very tiny spherical particles. The particles are aggregated via interparticle interactions mediated by the ionic liquid molecules and thus they form self-assembled nanostructure. The UHR TEM images of the materials are shown in Figure 4. The individual TEM images show that the present material is composed of very tiny nanocrystals of dimensions 3-4 nm. The nanocrystals are clearly visible in the TEM image Fig 4b. We have marked one individual nanocrystal. It is quite evident that the self-assembled structure was unchanged after sulfonation and calcinations [43]. The crystal fringes are clearly visible in this image. The corresponding FFT and SAED patterns are shown in Figures 4c and 4d, respectively [44].

#### Porosity and BET surface area:

The porosity, BET surface area and pore size distribution as well as pore volume of the sulphated zirconia was obtained from N<sub>2</sub> adsorption-desorption isotherm, which is shown in the Figure 5. The isotherm is a typical type IV adsorption-desorption isotherm, which is a characteristics of the mesoporous material. Pronounced desorption hysteresis present in the isotherm is an indicative of the presence of large mesopores in the material. The BET surface area calculated from the above isotherm in the P/P<sub>0</sub>=0.02-0.30 region was found to be 162 m<sup>2</sup> g<sup>-1</sup>. The pore size distribution employing NLDFT method revealed that this material has a peak pore width of 3.27 nm.

#### Surface acidity:

Surface acidity of the mesoporous sulphated zirconia has been estimated by the temperature programmed desorption of ammonia (TPD-NH<sub>3</sub>). TPD-NH<sub>3</sub> profile of M-IL-SZO-1C (Figure 6) indicates presence of moderately good acidic sites and desorption profile

is distributed from low to high temperature region. This desorption profile corresponds to the presence of both weak and strong acidity. Total acidity calculated from the profile is 0.71 mmol  $g^{-1}$ . We have also carried out the acidimetric titration to determine the surface acidity of the self-assembled sulphated zirconia material. The detailed experimental procedure and calculations are provided in the supporting information. From this titrimetric data we obtained 1.0 mmol  $g^{-1}$  surface acidity for M-IL-SZO-1C (supporting information), which is in close agreement with the TPD-NH<sub>3</sub> result. Due to this surface acidity suphated zirconia has been employed as a solid acid catalyst [45-46].

#### **Catalytic activity**

Self-assembled sulphated zirconia material has been employed as catalyst for the esterifiaction of long chain fatty acids using methanol as a solvent cum reactant. We have first studied the reaction of lauric acid with methanol at room temperature for 8 h. <sup>1</sup>H NMR analysis (supporting information Figure S3) suggested that the methyl laurate formation is not very promising. Only 30% conversion of lauric acid is observed after 8 h. But when we have increased the reaction temperature to 333 K the yield of the reaction reached 93.3%. So we have performed all the other catalytic reaction in 333 K temperature keeping the reaction time of 8 h. The reaction went well for all other long chain fatty acids as seen from Table 1. We have calculated mass balance for these esterification reactions. Our results suggested that ester production was quantitative with substrate conversion. The mass balance was >99% in all cases [47] and no adsorption on the catalyst surface occurred. The yields were moderate to high for all the substrates. The catalytic pathway for the esterification of FFA can be described by the mechanism shown below (Scheme 2).



**Scheme 2.** Probable mechanistic pathway for the catalytic esterification over mesoporous sulphated zirconia.

Here the  $-CO_2H$  moiety could interact with Zr(IV) sites of the catalyst leading to the activation of carbonyl carbon. This is followed by the attack of the alcohol and elimination of one molecule of water to yield the corresponding ester.

Das *et al* on the other hand has used mesoscopically assembled sulphated zirconia nanoparticles for these biodiesel synthesis, where the observed TOF ( $h^{-1}$ ) values for lauric acid, oleic acid and decanoic acids were in the range of 2.31-0.54 [29]. Santos *et al* used WOx/ZrO<sub>2</sub> catalysts for palmitic acid esterification and reported TOF ( $h^{-1}$ ) in the range of 3.2-9.5 [48]. In this context we have obtained much larger TOF ( $h^{-1}$ ) for the FAME conversion for different long chain fatty acids under optimized reaction conditions over sulphated zirconia catalyst M-IL-SZO-1C (TOF= 12.56-11.91  $h^{-1}$ ). This result suggested that

our sulphated zirconia material is a very efficient catalyst for the synthesis of biodiesel products.

### **Catalyst reusability**

To examine whether the self-assembled sulphated zirconia catalyst is heterogeneous and reusable we have carried out several experiments. After catalytic reaction we have filtered and recovered the catalyst. It was washed by methanol and hexane for several times in order to release the polar and non polar reactants and product trapped inside pore and surface of the catalyst. Then the catalyst was dried in an air oven for 3 h and then it is employed in the next cycle of catalytic reactions. The reusability test has been carried out for five consecutive cycles taking lauric and oleic acids as the model reactants. TOFs for different reaction cycles are shown in Figure 7. As seen from this plot that for both long chain fatty acids our self-assembled sulphated zirconia material showed very little loss in catalytic activity upto five reaction cycles. Further, we have analyzed the used catalyst M-IL-SZO-1C through TEM (Figure S17). From the electron microscopic images it is clear that morphology and particle size of M-IL-SZO-1C has been retained after five repetitive reaction cycles. This result suggests that our sulfonated zirconia material M-IL-SZO-1C is a very efficient and reusable heterogeneous catalyst for the synthesis of biodiesels.

In order to explore the heterogeneous nature of the sulfonated zirconia catalyst M-IL-SZO-1C, we have carried out the hot-filtration test. In this experiment the reaction allowed to continue under standardized reaction conditions and after 4 h the catalyst has been filtered from the reaction mixture under hot conditions. Then the filtrate is stirred at 333 K for another 4 h in absence of any catalyst. At the time of hot filtration product yield was 62.3%. 4 h after the hot filtration the progress of the reaction was negligible in absence of the catalyst and yield of methyl laurate remained almost same at 62.4%. This

result confirms that there is no leaching of sulphur from the catalyst to the reaction mixture and M-IL-SZO-1C acts as an ideal heterogeneous catalyst.

### Conclusions

From the above results we can conclude that ionic liquid can be successfully employed as a porogen to prepare self-assembled tetragonal mesoporous  $ZrO_2$ nanocrystalline material. Sulphonation of this zirconia material resulted sulphated mesoporous  $ZrO_2$ , which can be successfully employed as a recyclable heterogeneous catalyst for the esterifiaction of long chain fatty acids using methanol both as a reactant and solvent. The catalytic process is green and advantageous in terms of easy work-up and separation of the catalyst from the reaction mixture, reusability of methanol and retention of the catalytic activity for several reaction cycles. Synthesis and catalytic potential of nanotechnology based recyclable heterogeneous solid acid catalysis demonstrated herein is inherently advanced, economical and green for the production of a wide range of biodiesel products.

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Table 1. Esterification of different long chain fatty acids over M-IL-SZO-1C<sup>a</sup>



Fatty acid	Acid :	Product	Yield <sup>b</sup>	Weight of the	TOF (mols of
	MeOH		(%)	corresponding	acid
	(mmol)			methyl ester	converted
				(mg)	/mol of
					active site $(h^{-1})^{c}$
Lauric acid	1:30		93.3	199	11.91
Myristic acid	1:30		89.8	217	11.51

Palmitic acid	1:30		90.7	244	11.63
Stearic acid	1:30		88.9	265	11.39
Oleic acid	1:30	the second secon	74.7	221	9.58
Sebacic acid	1:30		98.0	225	12.56

<sup>a</sup>Reaction conditions: Long chain fatty acid (1 mmol), catalyst M-IL-SZO-1C (0.08g) and 0.96 g MeOH (30 mmol), reaction temperature (333 K), reaction time = 8 h.

<sup>b</sup>Yields are determined by <sup>1</sup>H NMR analysis.

<sup>c</sup>TOF based on 1.17 wt% of S determined by elemental analysis.

<sup>1</sup>H and <sup>13</sup>C NMR chemical shifts for methyl esters of different long chain fatty acids reported in table 1(respective spectra are shown in ESI: Methyl laurate [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>10</sub>-COOCH<sub>3</sub>]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 3.638 (3H, s); δ=2.293-2.256 (2H, t); δ= 1.610-1.575 (2H, t); δ= 1.259-1.235 (16H, m); δ= 0.870-0.836 (3H, t); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 174.39; 51.46; 34.20; 32.00; 29.70; 29.55; 29.43; 29.36; 29.25; 25.06; 22.77; 14.16.

**Methyl myristate** [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>12</sub>-COOCH<sub>3</sub>]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):δ= 3.638 ( 3H, s); δ= 2.294-2.256 (2H, t); δ= 1.611-1.576 (2H, t); δ= 1.260-1.24 (20H, m); δ= 0.872-0.88 (3H, t); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 174.40; 51.47; 34.21; 32.04; 29.79; 29.76; 29.71; 29.57; 29.47; 29.38; 29.28; 25.08; 22.79; 14.18.

**Methyl palmitate** [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>14</sub>-COOCH<sub>3</sub>]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 3.603 (3H,s);  $\delta$ = 2.261-2.224 (2H, t);  $\delta$ = 1.584-1.549 (2H, t);  $\delta$ = 1.235-1.210 (24H, m);  $\delta$ = 0.844-0.811 (3H, t); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): $\delta$ = 174.23; 51.33; 34.12; 33.98; 32.02; 29.77; 29.75; 29.69; 29.55; 29.46; 29.35; 29.24; 29.20; 25.02; 24.83; 22.76; 14.11.

**Methyl stearate** [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>16</sub>-COOCH<sub>3</sub>]: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ= 3.601 (3H, s); δ= 2.256-2.227 (2H, t); δ= 1.580-1.552 (2H, t); δ= 1.238-1.209 (28H, m); δ= 0.841-0.814 (3H, t); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ= 174.20; 51.31; 34.10; 32.01; 29.78; 29.74; 29.68; 29.54; 29.45; 29.35; 29.23; 25.01; 22.75; 14.09.

**Methyl oleate** [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>7</sub>-CH=CH-(CH<sub>2</sub>)<sub>7</sub>-COOCH<sub>3</sub>]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 5.344-5.293 (2H, m); δ= 3.636 (3H, s); δ= 2.326-2.260 (2H, m); δ= 2.046-1.967 (4H, m); δ= 1.609-1.581 (2H, m); δ= 1.320-1.25 (20H, m); δ= 0.879-0.84 (3H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 174.37; 130.25; 51.45; 34.08; 32.01; 29.87; 29.78; 29.69; 29.63; 29.55; 29.42; 29.36; 29.25; 29.23; 27.31; 25.73; 25.04; 22.77; 14.22.

**Methyl sebacate** [CH<sub>3</sub>OOC-(CH<sub>2</sub>)<sub>8</sub>-COOCH<sub>3</sub>]: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ= 3.559 (6H, s); δ= 2.211-2.181 (4H, m); δ= 1.525-1.497 (4H, t); δ= 1.203 (8H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ= 174.10; 51.30; 33.93; 28.96; 24.81.

% Conversion was estimated from <sup>1</sup>H NMR: [Peak area of one proton near 3.64 (for -CH<sub>3</sub> gr.) divided by that of one proton at 2.27 (-CH<sub>2</sub> gr.)]  $\times$  100.

### Caption for figures

Figure 1.	Wide angle powder XRD patterns of M-IL-ZO-1(a) and M-IL-SZO-1C (b)
Figure 2.	FT-IR spectra of the M-IL-ZO-1 and M-IL-SZO-1C.
Figure 3.	FE-SEM images of M-IL-ZO-1(a) and M-IL-SZO-1C (b).
Figure 4.	UHR-TEM images of M-IL-ZO-1.
Figure 5.	$N_2$ adsorption/desorption isotherms of M-IL-SZO-1C at 77 K. Pore size
	distribution (PSD) plot employing NLDFT model is shown in the inset.
Figure 6.	NH <sub>3</sub> -TPD profile of M-IL-SZO-1C.
Figure 7.	TOFs for different reaction cycles over self-assembled mesoporous sulphated
	zirconia in the esterification of lauric acid $(\bullet)$ and oleic acid $(\blacktriangle)$ .



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



**Graphical abstract**