# Fabrication of magnetically carbonaceous solid acids from banana peel for the esterification of oleic acid

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#### 1. Materials and chemicals

Crude BP was obtained from a local fruit market in Xi'an, China and thoroughly washed with distilled water for further use.  $FeCl_3 \cdot 6H_2O$  (97.0%),  $CH_3OH$ ,  $BaCl_2$ , NaCl, fuming sulphuric acid (20%), *n*-hexane, activated carbon (AC), phenolphthalein and ethanol were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). OA, methyl palmitate, commercial Amberlyst-15 and niobic acid were purchased from Sigma-Aldrich Corp. All chemicals were of analytical grade. Ultrapure water was produced by a Millipore purification system (Millipore, MA, USA) and used to prepare all aqueous solutions.

## 2. Physico-chemical characterizations

Fourier transform infrared spectroscopy (FTIR) spectra were measured using a Bruker Tensor 27 spectrometer with the KBr pellet technique in the range 400 to 4000 cm<sup>-1</sup>. Thermal gravimetric analysis (TGA) was carried out using an America TA Instruments Q50 thermoanalysis instrument in the temperature range 303-1273 K with a heating rate of 10 K min<sup>-1</sup>. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku D/Max-3C Xray diffractometer with Cu K $\alpha_1$  radiation ( $\lambda = 1.54$  Å) at 40 kV and 30 mA with an Inel CPS 120 hemispherical detector. Raman spectra were obtained using a Thermo Nicolet dispersive Raman spectrometer system, under  $\lambda_{exc} = 532$  nm laser excitation. Nitrogen adsorptiondesorption isotherms were measured at 77 K using a volumetric adsorption analyzer (Micromeritics ASAP 2020). Prior to analysis, the sample was automatically and manually degassed for 15 h and 4 h under vacuum at 573 K, respectively. The sample was then transferred to the analysis system where it was cooled in liquid nitrogen. The specific surface area  $(S_{\text{BET}})$  was calculated by the Brunauer-Emmett-Teller (BET) equation using adsorption data in a relative pressure range from 0.02 to 0.32; the total pore volume was evaluated by converting the adsorption volume of nitrogen at relative pressure 0.973 to the equivalent liquid volume of the adsorbate, and the micropore volume were obtained using the t-plot method. Pore size distributions (PSDs) were determined from the adsorption branches of the isotherms using nonlocal density functional theory (NLDFT) model. The pore size distributions for mesoporous were assessed by using Barrett-Joyner-Halenda (BJH) model.

Scanning electron microscopy (SEM) images were obtained on a FEI Quanta 200 scanning electron microscope at an accelerating voltage of 20 kV. A thin gold film was sputtered onto the samples before SEM measurements. The elemental compositions of the as-obtained materials were determined from energy dispersive X-ray (EDX) analysis attached with SEM. Transmission electron microscopic (TEM) images were conducted on a JEOL JEM-2100 microscope operated at 200 kV. Samples were first dispersed in ethanol and then collected on carbon-film-covered copper grids for analysis. The presence of different functional groups on the surface of MPCs-0.6, MPCs-0.6-SO<sub>3</sub>H, DPBP-SO<sub>3</sub>H MPCs-0.8-SO<sub>3</sub>H and 4 times used MPCs-0.8-SO<sub>3</sub>H were investigated using an Axis Ultra X-ray photoelectron spectrometer (XPS; Kratos Analytical Ltd.). Binding energies were calibrated using the contained carbon (C1s = 284.6 eV). Elemental analyses were carried out on an Elementar Vario EL III microanalyzer. The magnetic properties were measured MPMS-XL-7 using a superconducting quantum interference device magnetometer (SQUID, Quantum Design). The acid strength of the MPCs-0.6-SO<sub>3</sub>H and MPCs-0.8-SO<sub>3</sub>H catalysts were determined by CHEMBET-Palsar TPR/TPD (Automated Chemisorption Analyzer) instrument.

## 3. Acid site density

To quantify the density of acid functional groups on the surface of the catalysts, the acid site density was estimated by ion-exchange titration. The H<sup>+</sup> on the acid functional groups were firstly exchanged with Na<sup>+</sup> by immersing 0.05 g of the catalyst in 10 mL of 2 mol L<sup>-1</sup> NaCl solution at room temperature for 24 h under stirring (150 rpm). The H<sup>+</sup> concentration in the supernatant solution was expected to have equilibrated after this long contact time, and the solution was then titrated with standardized NaOH (0.01 mol L<sup>-1</sup>). Phenolphthalein was used to detect neutralization. The acid site density was calculated by the number of moles of NaOH titrated divided by the weight of the catalyst.

# 4. Esterification kinetics of OA with methanol

To further explore the catalytic activities of the as-prepared catalysts, the esterification kinetics of OA with methanol was investigated. The kinetic parameters were determined, using the Arrhenius equation, under the selected conditions. The reaction rate constants at

different temperatures were calculated assuming that the reaction proceeded according to first-order kinetics, with a final conversion of 100%. The reaction rate constant  $k_r$  was determined according to equation (1):

$$C(t) = C_f\left(1 - e^{-krt}\right) \tag{1}$$

where C(t) is the conversion (%) of OA at time t,  $C_f$  is the final conversion, assumed to be 100% (complete conversion),  $k_r$  is the reaction rate constant (min<sup>-1</sup>), and t is the time (min).

The activation energy  $(E_a)$  was determined by solving equations (2) and (3).

$$k_r = A e^{-E_a/RT}$$
 (2)  $\ln k_r = \ln A - \frac{E_a}{RT}$  (3)

where *A* is the pre-exponential factor (min<sup>-1</sup>),  $E_a$  is the activation energy (KJ mol<sup>-1</sup>), *R* is the gas constant, and *T* is the absolute temperature (K).

## 5. Catalyst reusability

To evaluate the reusability of the MPCs-*x*-SO<sub>3</sub>H, the esterification of OA was repeated four times. After each batch of the reaction, the catalyst was separated by using a permanent magnet from the solution and washed with alcohol, and dried at 50 °C. The dried catalyst was then reused for the next batch with the same conditions. For each batch, a fresh solution containing OA and methanol at the same concentrations as in the first batch was prepared.

|                            | Textual properties                |                                   |                       |                                   |           | <sup>[g]</sup> Chemical |                   |       |      |     |
|----------------------------|-----------------------------------|-----------------------------------|-----------------------|-----------------------------------|-----------|-------------------------|-------------------|-------|------|-----|
| Sample                     |                                   |                                   |                       |                                   |           | C                       | composition (wt%) |       |      |     |
|                            | <sup>[a]</sup> S <sub>BET</sub>   | $^{[b]}S_L$                       | $^{[c]}V_{b}$         | <sup>[d]</sup> V <sub>micro</sub> | [e] Pore  | [f] Meso                | Ν                 | С     | Н    | S   |
|                            | (m <sup>2</sup> g <sup>-1</sup> ) | (m <sup>2</sup> g <sup>-1</sup> ) | (cc g <sup>-1</sup> ) | (cc g <sup>-1</sup> )             | size (nm) | size (nm)               |                   |       |      |     |
| MPCs-0.2                   | 180.7                             | 272.9                             | 0.19                  | 0.07                              | 3.50      | 11.38                   | 1.67              | 64.88 | 1.92 |     |
| MPCs-0.4                   | 505.1                             | 671.5                             | 0.39                  | 0.18                              | 2.60      | 8.21                    | 1.39              | 56.08 | 1.68 |     |
| MPCs-0.6                   | 380.4                             | 505.1                             | 0.30                  | 0.14                              | 2.82      | 9.92                    | 2.13              | 51.84 | 2.32 |     |
| MPCs-0.8                   | 370.5                             | 492.3                             | 0.35                  | 0.13                              | 3.03      | 11.33                   | 1.23              | 42.58 | 1.79 |     |
| MPCs-1.0                   | 399.1                             | 532.7                             | 0.36                  | 0.10                              | 3.22      | 6.15                    | 1.07              | 39.56 | 1.46 |     |
| DPBP                       | 128.17                            | 171.03                            | 0.11                  | 0.06                              | 1.93      | 9.58                    | 1.67              | 69.87 | 2.89 |     |
| MPCs-0.2-SO <sub>3</sub> H | 156.7                             | 209.2                             | 0.17                  | 0.05                              | 3.54      | 11.40                   | 1.85              | 69.91 | 1.96 | 3.3 |
| MPCs-0.4-SO <sub>3</sub> H | 173.2                             | 237.1                             | 0.26                  | 0.06                              | 3.03      | 9.44                    | 1.50              | 59.55 | 1.70 | 3.7 |
| MPCs-0.6-SO <sub>3</sub> H | 1097.0                            | 1455.0                            | 0.74                  | 0.41                              | 2.35      | 6.06                    | 2.05              | 72.66 | 2.36 | 5.2 |
| MPCs-0.8-SO <sub>3</sub> H | 933.8                             | 1235.9                            | 0.57                  | 0.35                              | 3.29      | 8.81                    | 2.16              | 57.49 | 2.42 | 5.7 |
| MPCs-1.0-SO <sub>3</sub> H | 615.2                             | 825.3                             | 0.63                  | 0.15                              | 3.58      | 6.77                    | 1.45              | 53.31 | 1.81 | 2.8 |
| DPBP-SO <sub>3</sub> H     | 78.95                             | 106.53                            | 0.07                  | 0.05                              | 1.97      | 6.38                    | 2.12              | 78.31 | 2.37 | 1.3 |
| AC                         | 862.1                             | 973.2                             | 0.46                  | 0.31                              | 1.78      | 7.34                    |                   |       |      |     |
| AC-SO <sub>3</sub> H       | 574.4                             | 760.6                             | 0.31                  | 0.22                              | 1.99      | 4.13                    |                   |       |      | 2.5 |

**Table S1.** Textural properties and chemical compositions of MPCs-x and MPCs-x-SO<sub>3</sub>H prepared byusing Fe-based composite as precursor from BP

<sup>[a]</sup> BET surface area; <sup>[b]</sup> Langmuir surface area; <sup>[c]</sup> total pore volume; <sup>[d]</sup> microporous volume; <sup>[e]</sup> average pore size calculated from nonlocal density functional theory (NLDFT) method; <sup>[f]</sup> average mesoporous size calculated from BJH method using desorption data; <sup>[g]</sup> elemental analyses by combustion method.

| Catalyst                   | $E_{a}$                 |        | $k_r \ (10^{-3} \min^{-1})$ |       |       |       |  |
|----------------------------|-------------------------|--------|-----------------------------|-------|-------|-------|--|
| Cuturyst                   | (KJ mol <sup>-1</sup> ) | R      | 323 K                       | 333 K | 343 K | 353 K |  |
| MPCs-0.2-SO <sub>3</sub> H | 29.8                    | 0.9862 | 3.22                        | 3.74  | 6.15  | 8.67  |  |
| MPCs-0.4-SO <sub>3</sub> H | 27.7                    | 0.9974 | 1.56                        | 2.04  | 3.05  | 4.02  |  |
| MPCs-0.6-SO <sub>3</sub> H | 26.1                    | 0.9987 | 2.66                        | 3.56  | 5.01  | 6.55  |  |
| MPCs-0.8-SO <sub>3</sub> H | 29.4                    | 0.9986 | 3.14                        | 4.52  | 6.21  | 8.88  |  |
| MPCs-1.0-SO <sub>3</sub> H | 35.7                    | 0.9551 | 0.94                        | 1.98  | 2.68  | 3.44  |  |
| Amberlyst-15               | 37.7                    | 0.9483 | 0.71                        | 1.68  | 2.23  | 2.92  |  |
| $H_2SO_4$                  | 11.5                    | 0.9900 | 7.50                        | 8.51  | 9.32  | 11.41 |  |
| Blank                      | 70.5                    | 0.9744 | 0.0093                      | 0.035 | 0.05  | 0.13  |  |

Table S2. Kinetic parameters for the reaction of esterification of OA with methanol



Figure S1. Schematic illustration of fabrication of MPC-*x*-SO<sub>3</sub>H from natural BP



**Figure S2.** SEM images of (a) MPCs-0.2, (b, c) MPCs-0.2-SO<sub>3</sub>H, (d) MPCs-0.6, and (e, f) MPCs-0.6-SO<sub>3</sub>H, at different magnifications



Figure S3. SEM images of (a, b) MPCs-1.0, (c, d) MPCs-1.0-SO<sub>3</sub>H, (e) MPCs-0.6, (f-g) DPBP-SO<sub>3</sub>H, (h) DPBP and (i) BP, at different magnifications



**Figure S4**. XRD patterns of (a) MPCs-0.2 and MPCs-0.2-SO<sub>3</sub>H, (b) MPCs-0.4 and MPCs-0.4-SO<sub>3</sub>H, (c) MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H, (d) MPCs-0.8 and MPCs-0.8-SO<sub>3</sub>H, and (e) DPBP (unwashed)

and DPBP-SO<sub>3</sub>H



Figure S5. Energy dispersive X-ray (EDX) analysis of MPCs-0.2 (a, image A) and MPCs-0.2-SO<sub>3</sub>H (a, image B), MPCs-0.4 (b, image A) and MPCs-0.4-SO<sub>3</sub>H (b, image B), MPCs-0.6 (c, image A) and MPCs-0.6-SO<sub>3</sub>H (c, image B), MPCs-0.8 (d, image A) and MPCs-0.8-SO<sub>3</sub>H (d, image B), and MPCs-1.0 (e, image A) and MPCs-1.0-SO<sub>3</sub>H (e, image B), the Au is a film applied before SEM analysis to improve conductivity of MPCs-*x* and MPCs-*x*-SO<sub>3</sub>H.



**Figure S6**. Raman spectra of (a) MPCs-0.2 and MPCs-0.2-SO<sub>3</sub>H, (b) MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H, (c) MPCs-0.8 and MPCs-0.8-SO<sub>3</sub>H, and (d) MPCs-1.0 and MPCs-1.0-SO<sub>3</sub>H



Figure S7. TEM images of (a, b) MPCs-0.2 and (c-e) MPCs-0.2-SO<sub>3</sub>H at different magnifications



Figure S8. TEM images of (a, b) MPCs-0.6 and (c-e) MPCs-0.6-SO<sub>3</sub>H at different magnifications.



**Figure S9.** TEM images of (a, b) MPCs-0.8 and (c-d) MPCs-0.8-SO<sub>3</sub>H at different magnifications. Insert: high-resolution TEM image of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles in (d)



**Figure S10.** TEM images of (a) MPCs-1.0, (b-d) MPCs-1.0-SO<sub>3</sub>H, (e) high-resolution TEM image of a Fe<sub>3</sub>O<sub>4</sub> nanoparticle in (d), (f, g) DPBP-SO<sub>3</sub>H and (h) DPBP at different magnifications



Figure S11. TGA profile of MPCs-x-SO<sub>3</sub>H (x = 0.2, 0.4, 0.6, 0.8, 1.0) after calcination at 650 °C in air with a heating rate of 10 °C min<sup>-1</sup>

The original amount of Fe<sub>3</sub>O<sub>4</sub> in the MPCs-*x*-SO<sub>3</sub>H (x = 0.2, 0.4, 0.6, 0.8, 1.0) was evaluated by TGA analysis. Ultimately, the carbon became CO<sub>2</sub> gas and the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were oxidized into Fe<sub>2</sub>O<sub>3</sub> after combustion in air. The results demonstrated that the amount of Fe<sub>2</sub>O<sub>3</sub> was about 12.5 wt%, 22.2 wt%, 7.8 wt%, 18.9 wt% and 16.7 wt%, respectively. Thus, the Fe<sub>3</sub>O<sub>4</sub> amount was calculated to be approximately 12.08 wt%, 21.46 wt%, 7.54 wt%, 18.27 wt% and 16.14 wt% by weight accordingly.

To further validate the amount of iron oxide removed during the sulfonation process, the original amount of Fe<sub>3</sub>O<sub>4</sub> in the MPCs-*x* (x = 0.2, 0.4, 0.6, 0.8, 1.0) was also evaluated by TGA analysis. The results demonstrated that the Fe<sub>3</sub>O<sub>4</sub> amount was calculated to be approximately 20.18 wt%, 32.76 wt%, 47.14 wt%, 54.57 wt% and 73.44 wt% by weight accordingly (results are not shown). Thus it can be seen that the amount of iron oxide removed during the sulfonation process were 8.1 wt%, 11.3 wt%, 39.6 wt%, 36.3 wt% and 57.3 wt% accordingly. The ICP/AAS analysis further showed that the ratio of the amount of Fe<sup>3+</sup> removed during the sulfonation process and the original amount of Fe<sup>3+</sup> were 8.36%, 12.76%, 41.91%, 44.85% and 53.31% respectively, which are very close to the results of TGA analysis.



**Figure S12**. (a) C 1s XPS spectra of the MPCs-0.6, (b) N 1s XPS spectra of the MPCs-0.6, (c) O 1s XPS spectra of the MPCs-0.6, (d) distribution of C in MPCs-0.6, (e) distribution of Fe in MPCs-0.6, and (f) distribution of O in MPCs-0.6





**Figure S13.** FTIR spectra of (a) MPCs-0.2 and MPCs-0.2-SO<sub>3</sub>H, (b) MPCs-0.4 and MPCs-0.4-SO<sub>3</sub>H, (c) MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H, (d) MPCs-0.8 and MPCs-0.8-SO<sub>3</sub>H, and (e) MPCs-1.0 and MPCs-1.0 SO<sub>3</sub>H

The peak intensity of hydroxyl groups and carboxylic groups of MPCs-*x* at wavenumber of about 3430, 1640 and 1380 cm<sup>-1</sup>, C-H and C=O stretching of  $-CH_2$ -NH-CH<sub>3</sub> and carboxylic acid at wavenumber of ~2920 and 2850 cm<sup>-1</sup> [1], respectively. Besides, the adsorption bands appearing at between 950 and 650 cm<sup>-1</sup> that attributed to out-of-plane N-H deformation vibration of the aromatic compounds [2].

In comparison, the MPCs-*x*-SO<sub>3</sub>H cover relatively more peaks, apart from the 3430 or 3440 (O-H band), 2920 (C-H stretching vibration of -CH<sub>2</sub>-NH-CH<sub>2</sub> or -CH<sub>2</sub>-NH-CH<sub>3</sub>) [2], ~1635 and 1380 cm<sup>-1</sup> (C=O stretching of carboxylic acid and COO<sup>-</sup> anion stretching or aromatic-like C=C stretching mode in polyaromatic sketch [3]), and some new peaks founded at 1400, 1190, 1110, 1068, 1008 and 620 cm<sup>-1</sup>, which should be attributed to the stretching of C-S (1400 cm<sup>-1</sup>) [4], the symmetric stretching vibrations of S=O (1190 and 1110 cm<sup>-1</sup>) [5], the -SO<sub>2</sub>-symmetric stretching (1068 cm<sup>-1</sup>), the stretching vibrations of S=O bond (1008 cm<sup>-1</sup>) [6], the bending vibration of -OH groups hydrogen bonded to - SO<sub>3</sub>H groups (620 cm<sup>-1</sup>) [7], respectively. Although these peaks are observed in most spectra, they have weak intensities, due to the efficient IR adsorption ability of the carbon frameworks formed by the high temperature treatment [8]. These results indicate the successful introduction of sulfonic groups onto the framework of MPCs-*x* through the direct sulfonating treatment.



**Figure S14**. (a) N 1s XPS spectra of the MPCs-0.6-SO<sub>3</sub>H, (b) O 1s XPS spectra of the MPCs-0.6-SO<sub>3</sub>H, (c) C 1s XPS spectra of the DPBP-SO<sub>3</sub>H, (d) N 1s XPS spectra of the DPBP-SO<sub>3</sub>H, and (e) S 2p XPS spectra of the DPBP-SO<sub>3</sub>H

The N1s spectra in the MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H includes four peaks with differentiated binding energy values via deconvolution (Figures S12b and S14a). These peaks can be assigned to the nitrogen atoms in the forms of pyridinic nitrogen (N-6 at 398.1 eV, C-N), quaternary nitrogen (N-Q at 400.8 eV, N-(C)<sub>3</sub>), pyrrolic or pyridonic N (N-5 at 399.7 eV), and pyridine-N-oxide (N-X at 402.1 eV) [9]. Figures S12c and S14b shows the O1s spectrum of MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H, which can be deconvoluted into four peaks. The peak at 530.5 eV is assigned to Fe-O corresponding to the oxygen in Fe<sub>3</sub>O<sub>4</sub> [10], and the peak at 531.8 eV is ascribed to C-O-Fe [2], suggesting the linkage of Fe<sub>3</sub>O<sub>4</sub> with porous carbon through this bond. In addition, the peak at 532.6 eV is attributed to the Fe-OH or C-O-C [10, 11], and the peak at 533.7 eV is ascribed to C-OH and/or C-O-C groups [11]. The sample of MPCs-0.6-SO<sub>3</sub>H has more functional groups compared to DPBP-SO<sub>3</sub>H, which could be further indicated that the bottom-up strategy not only introduces magnetism and SO<sub>3</sub>H groups on the carbon matrix through in situ nucleation of  $Fe_3O_4$  and the formation of C-S bonds, but also modifies the surface of the materials with additional oxygenated functional groups (e.g., pyridine-N-oxide). These findings suggest that the MPCs-x will be a potential alternative to the use of transition metal-based oxygen evolution catalysts, due to the high oxygen evolution activity of the nitrogen/carbon materials is from the pyridinic-nitrogen-or/and quaternary-nitrogen-related active sites [12].



Figure S15. (a) Distribution of C in MPCs-0.6-SO<sub>3</sub>H, (b) distribution of C in DPBP-SO<sub>3</sub>H, (c) distribution of O in DPBP-SO<sub>3</sub>H, (d) distribution of S in DPBP-SO<sub>3</sub>H, (e) distribution of Fe in MPC-0.6-SO<sub>3</sub>H, (f) distribution of S in MPC-0.6-SO<sub>3</sub>H, and (g) distribution of O in MPC-0.6-SO<sub>3</sub>H



**Figure S16**. Nitrogen sorption isotherms and pore size distributions for (a, c) MPC-0.4 and MPC-0.4-SO<sub>3</sub>H, and (b, d) MPC-1.0 and MPC-1.0-SO<sub>3</sub>H



**Figure S17**. Nitrogen sorption isotherms and pore size distributions for (a-d) MPCs-0.2 and MPCs-0.2-SO<sub>3</sub>H, and (e-h) MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H. The figures of d and h corresponding to the size distributions from BJH model



Figure S18. Nitrogen sorption isotherms, pore size distributions and pore volume for (a-b) MPCs-0.8 and

MPCs-0.8-SO<sub>3</sub>H.



Figure S19. TGA curves of (a) MPCs-0.4, (b) DPBP, (c) MPCs-0.6, (d) MPCs-0.4-SO<sub>3</sub>H, (e) MPCs-

0.6-SO<sub>3</sub>H, and (f) DPBP-SO<sub>3</sub>H

TG analysis of MPCs-0.4 and MPCs-0.4-SO<sub>3</sub>H, MPCs-0.6 and MPCs-0.6-SO<sub>3</sub>H, DPBP and DPBP-SO<sub>3</sub>H were carried out at a heating rate of 10 K min<sup>-1</sup>. In all cases, two main weight losses are observed. The first step weight loss for all samples should be attributed to the volatilization of moisture at around 100 and 200 °C. The second step of the weight loss for MPCs-0.4 (or MPCs-0.6) and MPCs-0.4-SO<sub>3</sub>H (or MPCs-0.6-SO<sub>3</sub>H) between 450 and 1000 °C corresponded to the carbon phase in the Fe<sub>3</sub>O<sub>4</sub>/C composites begins to decompose [13] and the decomposition of SO<sub>3</sub>H groups to H<sub>2</sub>O and SO<sub>2</sub>. Compared to the initial weight, the MPCs-0.4 (57.25 wt%) and MPCs-0.4-SO<sub>3</sub>H (43.95 wt%), MPCs-0.6 (45.55 wt%) and MPCs-0.6-SO<sub>3</sub>H (35.23 wt%), DPBP (55.86 wt%) and DPBP-SO<sub>3</sub>H (19.78 wt%) weight losses are confirmed by the TG data. This is because the hydroxyl groups, carboxylic groups, sulfonic groups and iron oxide nanoparticles introduced into carbon-based materials are pyrolyzed upon exposure to inert atmosphere, presenting structural defects and impairing the thermal stability of MPCs-x and MPCs-x-SO<sub>3</sub>H at elevated temperatures. Obviously, the heat stability of MPCs-x-SO<sub>3</sub>H achieved a significant enhancing compared to DPBP-SO<sub>3</sub>H, which is very favorable for catalyst recycling. It can be speculated that the sulfonated MPCs-x exhibits an increased temperature for the major mass loss, due to sulfonation of the hydroxyl groups enhancing the thermal stability of the functional groups, preventing the emergence of structural defects in sufonated MPCs-x as the temperature increases [6]. The thermal stability changes of all of the samples also confirm that the functional groups are covalently anchored into the chemical structure of MPCs-x or DPBP rather than simply being adsorbed on the surface.



Figure S20. Mechanism model of MPC-x-SO<sub>3</sub>H formation



**Figure S21.** Arrhenius-type plots (a, b) for the esterification of OA with methanol. Reaction conditions: weight ratio of OA to methanol 1:33, catalyst loading of 3 wt%, reaction time of 3 h, at different reaction temperature



**Figure S22.** Water tolerances of MPCs-0.2-SO<sub>3</sub>H, MPCs-0.4-SO<sub>3</sub>H, MPCs-0.6-SO<sub>3</sub>H, MPCs-0.8-SO<sub>3</sub>H and Amberlyst 15 in esterification of OA and methanol at 80 °C for 2 h (a-c)



**Figure S23.** Reproducibility of MPCs-0.2-SO<sub>3</sub>H, MPCs-0.4-SO<sub>3</sub>H, MPCs-0.6-SO<sub>3</sub>H, MPCs-0.8-SO<sub>3</sub>H, and Amberlyst 15 for esterification of OA with methanol (weight ratio of OA to methanol 1:33,



catalyst loading of 3 wt%) at 80 °C for 8 h

**Figure S24.** XPS survey spectra of the fresh and 4 times reused MPCs-0.8-SO<sub>3</sub>H (a), and S 2p spectrum of the 4 times reused MPCs-0.8-SO<sub>3</sub>H (b)



**Figure S25.** Photographs showing the magnetic responsive performance of (a-c) MPCs-0.2-SO<sub>3</sub>H and (d) MPCs-0.8-SO<sub>3</sub>H by a permanent magnet at a different angle

Table S3. Recent typical examples of the use of sulfonated carbon-based catalyst in biodiesel

| Biodiesel production                             |   |  |  |   |  |   |  |  |  |
|--|---|--|--|---|--|---|--|--|--|
| Catalyst   | Sulfonated<br>mesoporous<br>carbon (MC)   | Sulfonated<br>ordered<br>mesoporous<br>carbons (OMC)   | Magnetic<br>solid acids  | OMC-H <sub>2</sub> O <sub>2</sub> -SO <sub>3</sub> H                          | SO <sub>3</sub> H-bearing<br>cellulose-derived<br>carbon solid<br>acids                                      | MPC- <i>x</i> -SO <sub>3</sub> H  |  |  |  |
| Preparation<br>method                            | Sulfonation of<br>MC via a soft-<br>template route  | Sulfonation of<br>MC via a<br>nanocasting<br>technique   | Sulfonation of<br>Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @C                                      | Sulfonation of<br>H <sub>2</sub> O <sub>2</sub> -treated<br>OMC               | Sulfonation of<br>incompletely<br>carbonized<br>microcrystalline<br>cellulose powder                         | Thermal<br>conversion of<br>Fe(III)-based<br>complexes and<br>subsequent<br>sulfonation                               |  |  |  |
| Feedstocks<br>Reaction<br>conditions<br>Activity | Oleic acid (OA)<br>Methanol-to-<br>OA molar ratio<br>= 30:1; 3 h; 70<br>°C; 0.1 g<br>catalyst<br>Yield (%) = 95 | OA<br>Ethanol -to-OA<br>molar ratio =<br>10:1; 10 h; 80<br>°C; 0.05 g<br>catalyst<br>Yield (%) = 69-<br>74 | OA<br>Methanol -to-<br>OA molar ratio<br>= 20:1; 5 h; 70<br>°C; 0.1 g<br>catalyst<br>Yield (%) = 60-<br>81 | OA<br>Methanol-to-OA<br>molar ratio = 20 :<br>1; 80 °C; 2 h<br>Yield (%) = 80 | OA<br>Methanol-to-OA<br>molar ratio = 26<br>: 1; 95 °C; 4 h;<br>catalyst amount<br>4  wt%<br>Yield (%) = 100 | OA<br>Weight ratio of<br>OA to methanol<br>was 1:33; 80 °C;<br>8 h; catalyst<br>amount 3 wt%<br>Yield (%) = 63-<br>94 |  |  |  |
| Recyclability<br>Separation<br>Ref.              | No obvious<br>decrease after 5<br>cycles<br>No<br>[14]  | Gradually<br>decreases after<br>two runs<br>No<br>[15]   | 5 times no<br>obvious<br>decrease<br>Yes<br>[5]  | No obvious loss<br>after 5 cycles<br>No<br>[16]                               | No obvious loss<br>after 5 cycles<br>No<br>[17]  | Slowly declined<br>after 4 cycles<br>Yes<br>This work   |  |  |  |

#### production

## References

- R.-L. Liu, Y. Liu, X.-Y. Zhou, Z.-Q. Zhang, J. Zhang and F.-Q. Dang, *Bioresource Technol.*, 2014, 154, 138-147.
- [2] G.-P. Hao, W.-C. Li, D. Qian and A.-H. Lu, Adv. Mater., 2010, 22, 853-857.
- [3] G. Chen and B. Fang, Bioresource Technol., 2011, 102, 2635-2640.
- [4] W.-J. Liu, K. Tian, H. Jiang and H.-Q.Yu, Sci. Rep., 2013, 3, 2419.
- [5] B. Chang, Y. Tian, W. Shi, J. Liu, F. Xi and X. Dong, RSC Adv., 2013, 3, 20999-21006.
- [6] L. Wang, D. Wang, S. Zhang and H. Tian, Catal. Sci. Technol., 2013, 3, 1194-1197.
- [7] R. Xing, N. Liu, Y. Liu, H. Wu, Y. Jiang, L. Chen, M. He and P. Wu, Adv. Funct. Mater., 2007, 17, 2455-2461.
- [8] K. Nakajima and M. Hara, ACS Catal., 2012, 2, 1296-1304.
- [9] Z. Li, Z. Xu, X. Tan, H. Wang, C.M.B. Holt, T.J. Stephenson, B.C. Olsen and D. Mitlin, Energy

Environ. Sci., 2013, 6, 871-878.

- [10] L. Li, G. Zhou, Z. Weng, X.-Y. Shan, F. Li and H.-M. Cheng, Carbon, 2014, 67, 500-507.
- [11] M. Sevilla and A.B. Fuertes, *Chem. Eur. J.*, 2009, **15**, 4195-4203.
- [12] Y. Zhao, R. Nakamura, S. Nakanishi and K. Hashimoto, Nat. Commun., 2013, 4, 1-7.
- [13] J.-D. Xiao, L.-G. Qiu, X. Jiang, Y.-J. Zhu, S. Ye and X. Jiang, Carbon, 2013, 59, 372-382.
- [14] B. Chang, J. Fu, Y. Tian and X. Dong, RSC Adv., 2013, 3, 1987-1994.
- [15] R. Liu, X. Wang, X. Zhao and P. Feng, Carbon, 2008, 46, 1664-1669.
- [16] B. Chang, J. Fu, Y. Tian and X. Dong, J. Phys. Chem. C, 2013, 117, 6252-6258.
- [17] F. Su and Y. Guo, Green Chem., 2014, 16, 2934-2957.