

Supplementary Information

Sulfonated Hollow Sphere Carbon as an Efficient Catalyst for Acetalisation of Glycerol

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Synthesis of SiO₂@resin. SiO₂@resin was synthesized under Stöber conditions in a 100-ml flask. As a typical run, 25.32 mmol of NH₃·H₂O was added to the mixture of 27.7 g EtOH and 17.4 g of water, stirring at room temperature for 10 min. After increasing the temperature to 30 °C in an oil bath, 7.94 mmol of tetraethyl orthosilicate (TEOS) was added and stirred for 10 min. Then, 2.23 mmol of resorcinol and 4.46 mmol of formaldehyde were alternatively added into the mixture, stirring at 30 °C for 24 h and subsequently at 100 °C for another 24 h under static conditions. After centrifugation, washing by a large amount of water and EtOH, and drying, the SiO₂@resin was obtained.

Synthesis of HSC-SO₃H. As a typical run, SiO₂@resin was heated under N₂ at 650 °C for 2 h to obtain SiO₂@HSC at first. After washing SiO₂@HSC (2 g) by 40 ml hydrofluoric acid (10-15%) at room temperature for three times for removing SiO₂, HSC sample was obtained. After evacuation HSC (1 g) at 100 °C for 3 h in a 200-ml flask, the mixture of CH₂Cl₂ (50 ml) and chlorosulfonic acid (10 ml) was added into

HSC in a flask at 0 °C, stirring for 12 h under N₂ atmosphere. After filtering, washing with a large amount of water and dioxane, and drying, the HSC-SO₃H sample was finally obtained. For comparison, SBA-15-SO₃H and Sn-MCM-41 were synthesized according to the literature [1,2].

Sample characterization. IR spectra were recorded using a Bruker 66V FTIR spectrometer. XPS spectra were performed on a Thermo ESCALAB 250 with Al K α radiation at $\theta=90^\circ$ for the X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 150 °C before the measurements. The pore-size distribution was calculated using the DFT model. CHNS elemental analysis was performed on a Perkin–Elmer series II CHNS analyzer 2400. The acid density was measured by acid-base titration with NaOH solution. Thermogravimetric analysis (TG) was performed on a Perkin-Elmer TGA7 and a DTA-1700 in flowing air. Scanning electron micrograph (SEM) images were performed on Hitachi SU-1510 electron microscopes and JEOL electron microscopes (FE-JSM 6700, Japan). Transmission electron microscope (TEM) images were performed using a Hitachi HT-7700.

Catalytic tests. The catalytic reactions were performed in a 100-ml glass reactor with a magnetic stirrer (1200 rpm). Typically, the acetone, catalyst, and solvent were mixed in the reactor. Then the reaction system was heated to a given temperature (the temperature was measured with a thermometer in an oil bath) and glycerol was introduced. After the reaction, the product was taken out from the reaction system and analysed by gas chromatography (GC-17A and GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17, OV-1, and FFAP) using dodecane as internal standard. The recyclability of the catalyst was tested by separating it from the reaction system by centrifugation, washing with large quantity of methanol and water, drying at 60 °C, then the catalyst was reused in the next reaction.

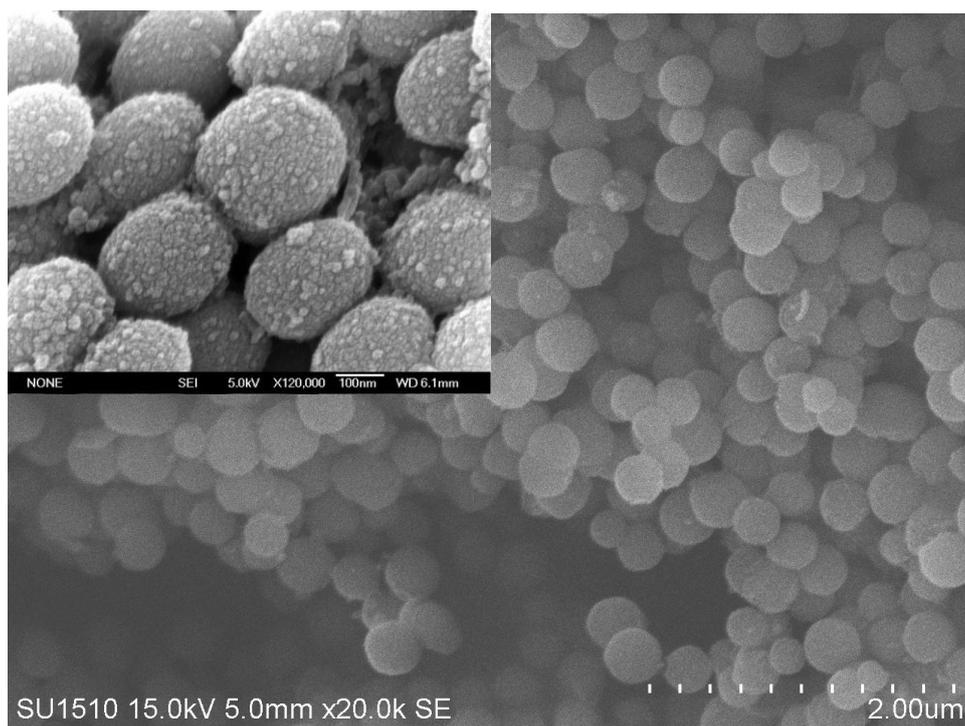


Figure S1. SEM image of HSC-SO₃H (Insert: Enlarged SEM image).

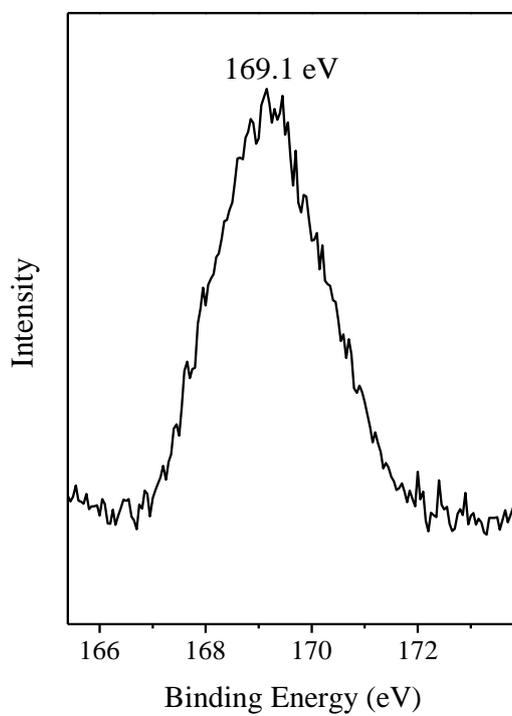


Figure S2. S₂p XPS spectrum of HSC-SO₃H

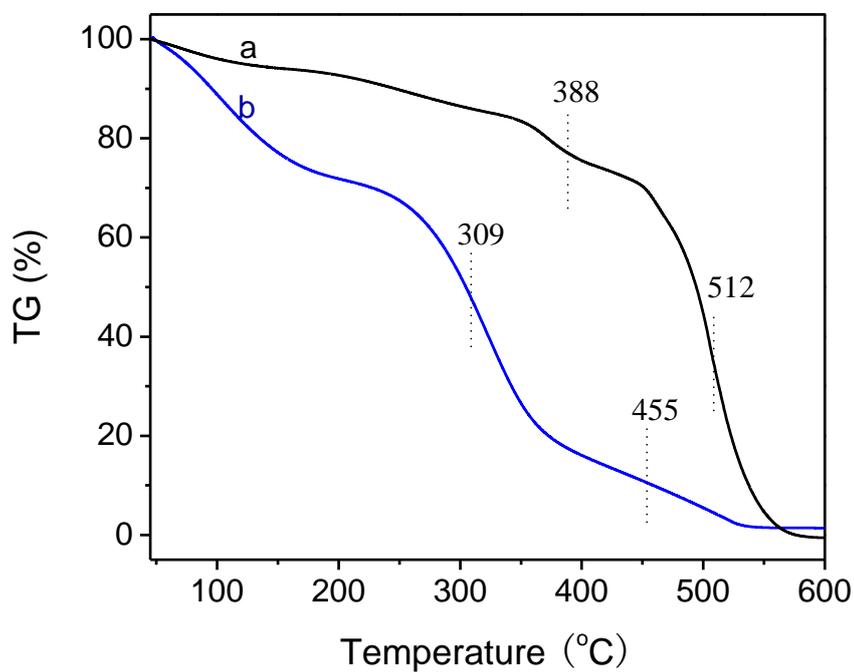
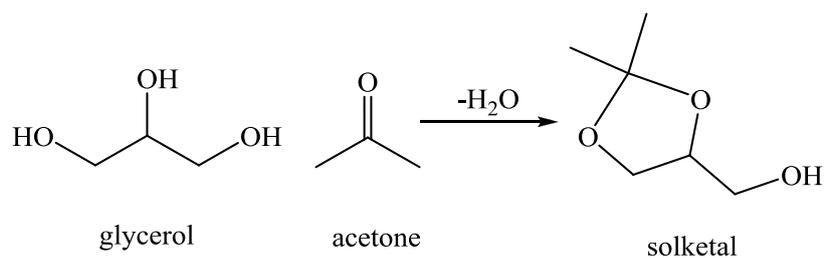
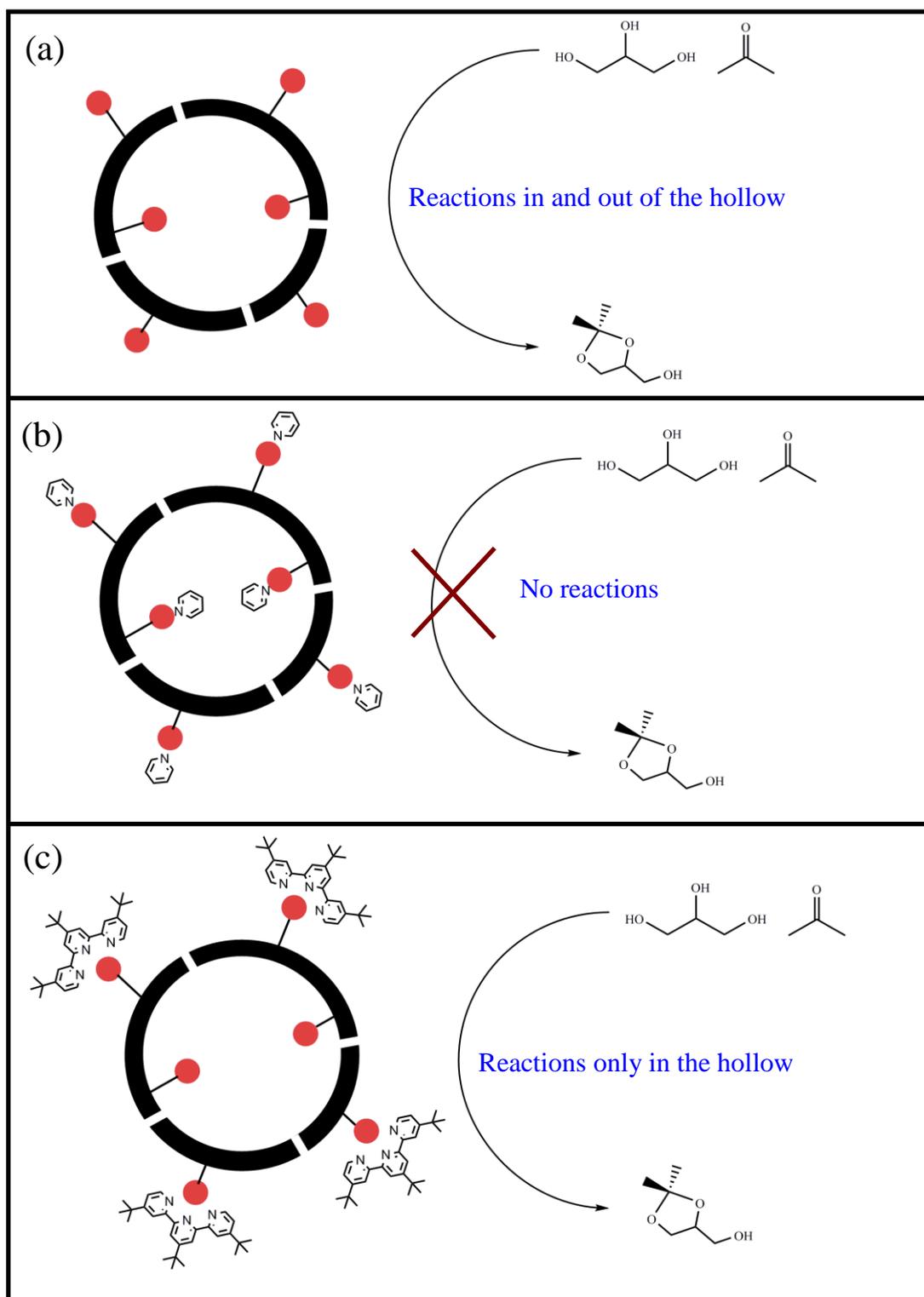


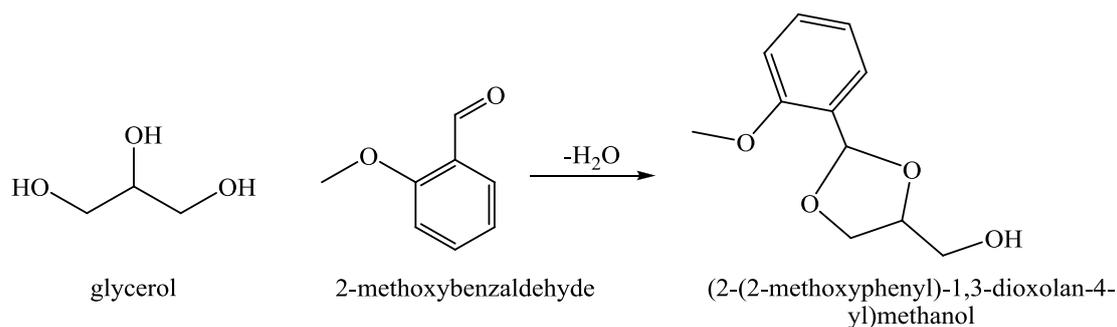
Figure S3. TG curves of (a) HSC-SO₃H and (b) Amberlyst-15.



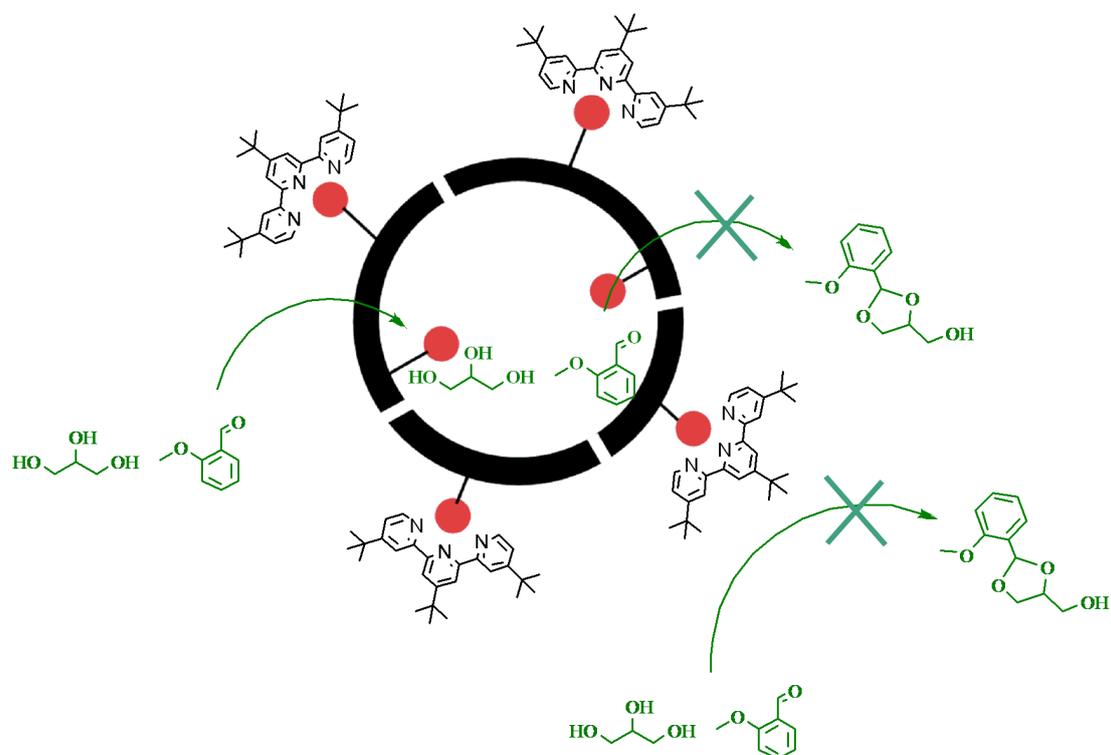
Scheme S1. The acetalisation of glycerol and acetone to produce solketal.



Scheme S2. Acetalisation of glycerol with acetone to solketal over (a) HSC-SO₃H, (b) Pyridine-poisoned HSC-SO₃H, and (c) Tri-pyridine-poisoned HSC-SO₃H.



Scheme S3. The acetalisation of glycerol and 2-methoxybenzaldehyde to produce (2-(2-methoxyphenyl)-1,3-dioxolan-4-yl)methanol.



Scheme S4. Acetalisation of glycerol and 2-methoxybenzaldehyde over tri-pyridine-poisoned HSC-SO₃H. The internal acid sites failed to catalyze the reaction, because the bulky molecule could not pass through the micropores on the carbon shell; the external acid site also failed to catalyze the reaction, because the external acid sites are completely poisoned by tri-pyridine.

Table S1. Acetalisation of glycerol to solketal over HSC-SO₃H and poisoned HSC-SO₃H catalysts.^a

Entry	Catalyst	Additive	Conversion (%)	Yield (%)	TOF (h ⁻¹)
1	HSC-SO ₃ H ^b	--	79.1	78.5	13.9
2	HSC-SO ₃ H ^c	Pyridine	4.5	4.5	--
3	HSC-SO ₃ H ^c	Tri-pyridine	76.0	75.0	13.3

^a Reaction conditions: 10 mmol of glycerol, 10 mmol of acetone, 4 g of *t*-BuOH, 0.1 mmol of additive, and the temperature of oil bath at 80 °C for 6 h; ^b 50 mg catalyst; ^c 100 mg catalyst. With the addition of tri-pyridine, half of the acid sites on HSC-SO₃H were poisoned; therefore two times of catalyst amount (100 mg) was used.

Table S2. Acetalisation of glycerol and 2-methoxybenzaldehyde over HSC-SO₃H and poisoned HSC-SO₃H catalysts.^a

Entry	Catalyst	Additive	Conversion (%)	Yield (%)
1	HSC-SO ₃ H ^b	--	66.0	66.0
2	HSC-SO ₃ H ^c	Pyridine	5.0	4.6
3	HSC-SO ₃ H ^c	Tri-pyridine	5.9	4.7

^a Reaction conditions: 10 mmol of glycerol, 10 mmol of 2-methoxybenzaldehyde, 4 g of *t*-BuOH, 0.1 mmol of additive, and the temperature of oil bath at 80 °C for 6 h; ^b 50 mg catalyst; ^c 100 mg catalyst. With the addition of tri-pyridine, half of the acid sites on HSC-SO₃H were poisoned; therefore two times of catalyst amount (100 mg) was used.

References:

1. D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka, G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2448.
2. L. Li, T. I. Koranyi, B. F. Sels, P. P. Pescarmona, *Green. Chem.*, 2012, **14**, 1611.