

Electronic Supplementary Information

Direct synthesis of sulfonated mesoporous SiO₂-TiO₂-SO₃H materials as solid acid catalysts

Hyang Im Ryoo^a, Lan Young Hong^a, Sang Hee Jung^a and Dong-Pyo Kim^{a,b*}

^a Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Yuseong Gu, Daejeon 305-764, Korea.

^b Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon 305-764, Korea

Fax: 82-42-823-6665; Tel: 82-42-821-6695; E-mail: dpkim@cnu.ac.kr

1. Preparation of sulfonated mesoporous materials

Sulfonated mesoporous hydrophilic materials were prepared using a modification of a consecutive sol-gel based reaction reported elsewhere. Tetraethylorthosilicate (TEOS) was prehydrolyzed in an ethanol-water mixture (2 to 1 volume ratio) containing HCl at 60 °C. The nonionic triblock copolymer, Pluronic P₁₂₃ (EO₂₀PO₇₀EO₂₀), was dissolved in ethanol and added to the TEOS sol. The titania sols were prepared by adding TiCl₄ to a ethanol/water(1/4 volume ratio) at room temperature. SiO₂-TiO₂ mesoporous composite sols were prepared by mixing the silica and titania sols at various ratios, which was followed by stirring for 2 hrs. Various amounts of the 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt (Tiron[®], Aldrich) were then added to the homogenous SiO₂-TiO₂ mesoporous composite sols, resulting in transparent dark orange solutions. The mesoporous SiO₂-TiO₂-SO₃H materials (SP series) were dried at 100 °C for 18 hrs, and then the surfactant incorporated in the mesoporous materials was removed by enough washing with ethanol for 6 hrs. For the comparison, a mixture of mesoporous SiO₂ sol and Tiron[®] was prepared by identical method as the above except the addition of TiCl₄. Alternatively, inorganic-organic hybrid hydrophilic resins (HP series) were prepared by mixing SiO₂-TiO₂-SO₃H mesoporous composite sols with the desired amount of 3-(methacryloyloxy)propyl trimethoxysilane (MPTMS) and polyethylene glycol dimethacrylate (PEG-DMA), respectively, followed by stirring for 3 hrs. The resulting products were dried under the same conditions used for the SP series. The SiO₂-TiO₂-SO₃H solid particles in Table 1 were washed with deionized water for sodium ion exchange with protons.¹

Table S1. Preparation of various SiO₂-TiO₂-SO₃H samples

Sample code	Composition (molar ratio)				
	TEOS	TiCl ₄	Tiron	MPTMS	PEG-DMA
1SP-1T	1	0.1	0.025	0	0
1SP-4T	1	0.1	0.1	0	0
1HP-1T	1	0.1	0.025	0.88	0.416
1HP-4T	1	0.1	0.1	0.88	0.416
2SP-1T	1	0.2	0.025	0	0

2. Characterization of sulfonated mesoporous materials

The infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer 400~4000 cm⁻¹. The small-angle X-ray diffraction (XRD) patterns of the powder samples were obtained on a RIGAKU model D/MAX-2500 X-ray diffractometer using Cu K α radiation at an accelerating voltage 40 kV and applied current of 30 mA, over the 2 θ range, 0.3°~5°. Transmission electron microscopy (TEM) was performed on a Philips, CM20 microscope coupled with energy dispersive x-ray (EDX) apparatus, X-ray fluorescence spectrometer (RIX2100, RIGAKU) and elementary analysis (Flash EA1112) were carried out to determine the composition of the samples. The Brunauer-Emmett-Teller (BET) surface area was measured by N₂ adsorption on a Micrometrics ASAP2010. The acid density of the sulfonic group incorporated mesoporous materials was determined using aqueous solution of sodium chloride (NaCl, 2 M) as an exchange agent. The resulting suspension was allowed to equilibrate and titrated by drop-wise addition of 0.01 M NaOH (aq) using a potentiometer. TGA-DTA measurements were carried out using a thermogravimetric/differential thermal analyzer (Perkin Elmer's Pyris Diamond) at a heating rate of 10 °C min⁻¹ under a flow nitrogen atmosphere. The optical transmittance of the solution was measured using a SINCO (UV S-2100) UV/vis spectrophotometer. The textural properties of the mesoporous materials were measured using the BET procedure. Nitrogen adsorption-desorption isotherms were taken at 77 K using a Micromeritics ASAP 2020 system. The pore size distributions were calculated using the BJH algorithm. The surface properties of the cured films on the glass substrates exhibits were analyzed by measurement of the contact angle with deionized water (DSA100 tensiometer, Krüss, Hamburg, Germany).

3. Catalytic esterification reaction

An esterification reactions of several carboxylic acids such as acetic acid, propanoic acid, butanoic acid, palmitic acid, lauric acid and oleic acid with ethanol were carried out using the sulfonated mesoporous hydrophilic materials as solid acid catalysts in the batch reactor. A round-bottomed glass flask was charged with 17 mmol of the carboxylic acids and 153 mmol of ethanol. The effect of the catalyst loading was examined. 0.1 g of a catalyst was added to the mixture, which was then kept at 80 °C for various periods. The aliquots separated at different time intervals were analyzed by gas chromatography (Model No. 5890, Hewlett-Packard) equipped with a flame ionization detector and a HP-5 capillary column coated with dimethylpolysiloxane as a stationary phase. The dodecane was used as an internal standard.

4. Elemental analysis data

Table S2. Experimental elemental ratio (wt %) of various SiO₂-TiO₂-SO₃H mesoporous materials

	Si	Ti	S	C	H	O	Molar ratio	
							Ti/Si	S/Ti
1SP-1T	37.84	6.47	2.12	2.47	0.20	50.89	0.1(0.1)	0.49 (0.5)
1SP-1T ^a	35.93	6.14	1.52	2.92	0.28	53.21	0.1(0.1)	0.37(0.5)
1SP-4T	30.44	5.21	6.96	7.83	0.65	48.92	0.1(0.1)	2.00(2.0)
1HP-1T	11.48	0.97	0.30	46.81	7.43	33.01	0.049(0.053)	0.47(0.5)
1HP-4T	10.98	0.94	1.15	46.16	7.22	33.55	0.050(0.053)	1.83(2.0)
2SP-1T	34.16	11.68	1.95	2.20	0.18	49.83	0.197(0.2)	0.25(0.25)

1SP-1T^a: Sample after first reaction, (): Theoretical value

5. N₂ adsorption-desorption isotherm and pore diameter distribution curves

The below curves showed a typical mesoporous hysteresis behavior in the pressure region of p/p_0 0.4~0.85, and also the total adsorbed volume of each curve is proportional to the surface area of each sample.

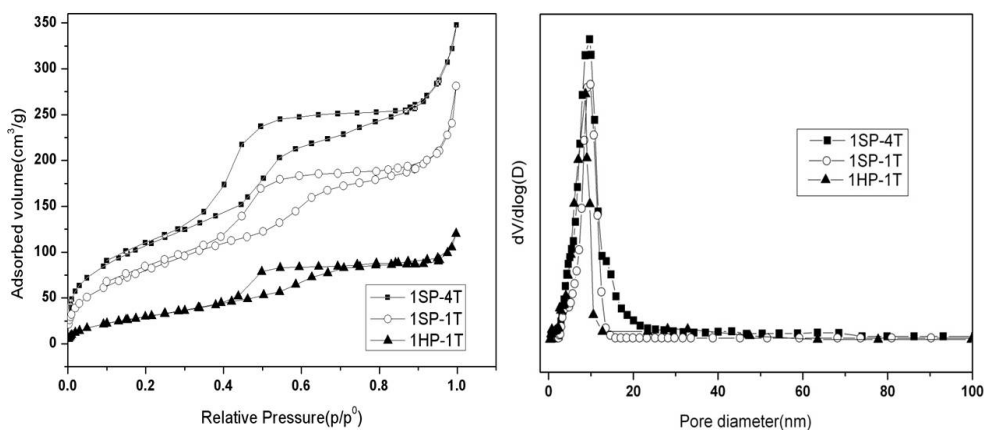


Figure S1. N₂ adsorption-desorption isotherms and pore diameter distribution curves of SiO₂-TiO₂-SO₃H materials

6. TGA –DTA thermogram

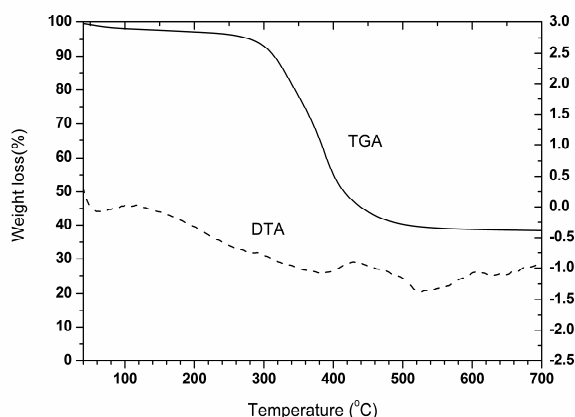


Figure S2. The TGA data of 1SP-4T materials

In 1SP-4T sample, the first stage loss of approximately 4% was due to the removal of volatile materials, such as water and ethanol up to 300 °C and next stage loss corresponded to the decomposition of organic material. This indicates that the binary $\text{SiO}_2\text{-TiO}_2$ oxides containing Tiron[®] $(\text{OH})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2$ on the surface were stable up to 300 °C.

7. UV absorption spectrum

The homogenous $\text{SiO}_2\text{-TiO}_2$ mesoporous composite sols turned to a red-orange color by adding Tiron[®] $(\text{OH})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2$ as a catecholic compound containing a sulfonate group. And the observed intense absorption band at 440 nm was originated from the chelation chemistry with Ti-catechol charge transfer.⁴ However, the only SiO_2 sols showed no color change in the presence of $(\text{OH})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2$, as seen in the below UV spectrum

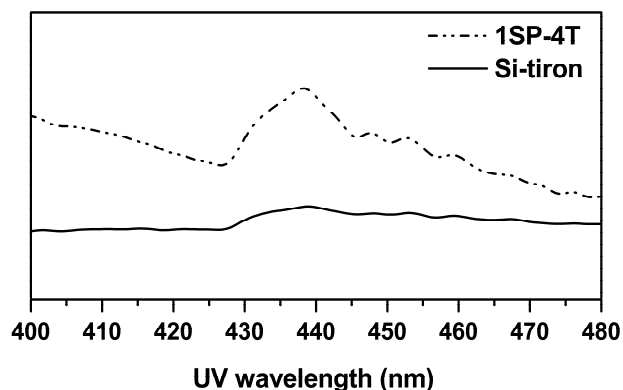


Figure S3. Comparative UV spectrum of $\text{SiO}_2\text{-TiO}_2\text{-SO}_3\text{H}$ sample (1SP-4T) and a mixture of mesoporous SiO_2 and Tiron[®] $(\text{OH})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2$.

8. FT-IR spectrum

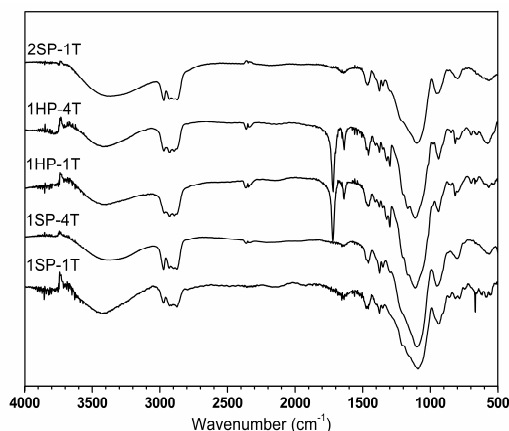


Figure S4. IR spectrum of various mesoporous SiO₂-TiO₂-SO₃H samples.

All samples showed a peak at ~940 cm⁻¹ corresponding to the Si-O-Ti stretching vibration. The O-H stretch and vibrations of the surface hydroxyl groups and physisorbed water were observed as a broad peak at 3000-3700 cm⁻¹. The bands at around 2850 and 2950 cm⁻¹ were assigned to the symmetric and asymmetric stretching modes of the C-H groups. The peaks around 1000-1250 cm⁻¹ were attributed to the asymmetric stretching of Si-O-Si groups. The C=O stretching bands were observed at 1710 cm⁻¹ and the peaks at 1630 cm⁻¹ were assigned to C=C groups in the HP series.²⁻⁵

References

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