Direct syntheses of sulfonated mesoporous SiO₂-TiO₂-SO₃H materials as solid acid catalysts[†]

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A facile one-step approach for a mesoporous solid acid catalyst SiO_2 - TiO_2 - SO_3H network was developed by the simple chelation of a benzene disulfonate compound to the Ti ion. The resulting catalyst showed excellent catalytic performance for esterification.

There is an increasing need for eco-friendly and efficient catalysts due to global legislation for environmental protection. Solid acids have attracted interest as environmentally benign catalysts in most chemical processes because of their advantages over homogeneous acids, such as non-corrosive, easy separation by filtration, and less waste production through recycling. Various insoluble solid acids have been reported to increase catalytic activity, and zeolites are considered to be good alternative acid catalysts owing to their large surface area.1 However, the small pore size in the 20 Å range makes them unsuitable for reactions involving bulky substrates. More desirable is a large regular pore structure of mesoporous solids with stronger Brønsted and/or Lewis acidity. The sulfonic acid-functionalized mesoporous silica provides a way of reinforcing the Brønsted acidity of solid acid, and has been used for a variety of chemical reactions, such as esterification. The SO₃H moieties on the surface of the ordered mesoporous MCM-41, SBA-15, and Ph-SO3H are mostly incorporated by a two-step process2: co-condensation or anchoring of -SH containing alkoxide precursors and subsequent oxidation in the presence of H_2O_2 or a post-modification grafting route,³ which are somewhat complicated and often incomplete. Therefore, a simpler synthesis technique that produces the mesostructure and the sulfonic acid sites simultaneously is needed.

Here, we propose a facile one-step approach for the incorporation of benzene disulfonate into a mesoporous SiO_2 -TiO₂ surface, thereby opening a path to aromatic acid-functionalization with multiple acid sites. The key synthetic approach is the chelation of a catecholic compound including two sulfonate groups, (OH)₂C₆H₂(SO₃Na)₂, on robust mesoporous networks, as illustrated in Scheme 1. This one-pot aromatic acid-functionalization of mesoporous oxide support is illustrated with esterification reactions under a variety of conditions. In particular, it is expected that the incorporation of an aromatic sulfonic acid with a more electron withdrawing phenyl group would increase the acidic strength of the resulting mesoporous material significantly, compared with the traditional aliphatic sulfonic acidfunctionalized samples.⁴

experimental details. See DOI: 10.1039/c0jm01174f



Scheme 1 (a) A synthetic diagram of sulfonated mesoporous network and (b) sulfonation chemistry of the SiO_2 -TiO₂ structure *via* catecholic chelation.

Pure inorganic SiO₂-TiO₂-SO₃H mesoporous materials, labeled as SP series, were prepared by binary sol–gel reactions, involving separate pre-hydrolysis of tetraethylorthosilicate (TEOS) with a triblock copolymer surfactant (Pluronic P_{123}) for the silica sol and that of TiCl₄ for the titania sol, mixing of the two sols at Ti : Si mole ratios of 0.1 and 0.2 for further reaction, and incorporating disodium 4,5-dihydroxy-1,3-benzene disulfonate (Tiron[®]) into the binary SiO₂-TiO₂ network. Inorganic–organic hybrid mesoporous materials, labeled HP series, were also synthesized by mixing the aforementioned SiO₂-TiO₂-SO₃H composite sols with 3-(methacryloyloxy)-propyl trimethoxysilane (MPTMS) and polyethylene glycol dimethacrylate (PEG-DMA) to improve the mechanical reliability.

The elemental analysis results in Table 1 show that the SO_3H/Ti ratios of the samples are stoichiometrically consistent with the initial compositions of the precursors. These binary SiO_2 -TiO₂ mesoporous structures were characterized by small-angle X-ray diffraction, as shown in Fig. 1. The unhybridized 1SP specimen with a Ti-to-Si ratio of 0.1 showed typical diffraction patterns of a SBA15-like hexagonal

Table 1Experimental S/Ti elemental ratio, BET surface area, aciddensity, catalytic activity and turn over frequency (TOF) of variousSiO2-TiO2-SO3H mesoporous materials

Sample code	S/ Ti ratio	BET (m ² /g) [pore vol. (cm ³ /g)]	Acid density (meq H ⁺ /g)	Yield (%)	Time (h)	TOF
1SP-4T	2.00	404 [0.40]	1.08	97	1	150
1SP-1T	0.49	313 [0.32]	0.30	97	5	107
2SP-1T	0.25	4 [0.01]	0.21	97	10	77
1HP-4T	1.83	58 [0.05]	0.14	90	12	89
1HP-1T	0.47	120 [0.15]	0.08	73	18	86

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Fig. 1 (a) Small-angle XRD patterns of the sulfonated mesoporous samples with different chemical compositions, and (b) TEM image of mesoporous 1SP-1T sample.

structure, which shows a high intensity (100) peak at 0.88° and additional higher order (110) peaks at 1.72°. This d(100) spacing of 9.8 nm indicates the formation of highly ordered mesoporous SiO₂-TiO₂ binary networks with pores, approximately 10 nm in diameter, which is relatively larger than the 2-7 nm reported for mesoporous silica.² The transmission electron microscopy (TEM) image of 1SP-1T (see ESI[†] for notation) in Fig. 1(b) also supports the presence of a highly ordered structure with no segregated SiO₂ and TiO₂ phases. However, the incorporation of an organic moiety such as MPTMS and PEG-DMA caused microstructural changes with peak broadening as well as a slight shift in the (100) peak to a lower diffraction angle, while the processability and toughness of the hybrid resin were enhanced. The change in this peak suggests that the pore size was made larger with slight disordering while maintaining the hexagonal pore structure. Interestingly the mesoporous SiO₂-TiO₂ skeleton was preserved even with a high organic content (ca. 50 mol%), whereas previous work reported a restriction on the organic content due to the collapse of the mesoporous structure that occurs for contents larger than 20 mol%.5

On the other hand, the peak intensities were reduced significantly when the titania portion was increased to a Ti : Si ratio of 0.2, as shown in Fig. 1(a), presumably due to lack of homogeneity, *i.e.* disordering of the network structure. Table 1 lists the surface areas from BET adsorption measurements. 1SP-4T and 1SP-1T show BET surface areas of 404 and 313 m²/g, respectively, which are relatively smaller than those of pure SiO₂ mesoporous materials with a similar pore size⁵ (see ESI† Fig. S1). This suggests that an increase in the Ti content or the incorporation of organic components caused a significant decrease in surface area, which is consistent with the partial collapse or decreased structural order. In addition, the TGA-DTA thermograms showed high thermal stability of the 1SP sample with only 4 wt% weight loss below 300 °C due to the adsorbed moisture and volatile organic portion (see ESI† Fig. S2).

A catecholic compound (dihydroxy benzene) can be readily chelated to Ti ions.⁶ In this study, chelation chemistry was introduced for the direct synthesis of a SiO₂-TiO₂-SO₃H network by coordinating 4,5-dihydroxy-1,3-benzene disulfonate, $(OH)_2C_6H_2(SO_3Na)_2$, as a catecholic compound containing a sulfonate group to a Ti atom. Under the acidic conditions of the sol–gel reaction, chelation was facilitated due to the conversion of the catecholic salt to a phenolic form as reported previously.⁷ This chelation turned the solution to a red-orange color due to Ti–catechol charge transfer, which was confirmed by the intense absorption at 440 nm (see ESI† Fig. S3). On the other hand, all samples showed optical transparency with a yellow

tint as well as a peak at ~940 cm⁻¹ corresponding to the Si-O-Ti stretching vibration, as measured by FT-IR spectroscopy⁸ (see ESI[†] Fig. S4). This confirms that there is no phase separation of the inorganic and organic moieties. This homogeneity also indirectly supports the stoichiometric coordination of catechols to Ti atoms. It should be noted that a benzene disulfonated mesoporous network was formed directly for the first time using a facile one-step sol–gel reaction. It is most likely that the surface of the binary mesoporous SiO₂-TiO₂ network structure was coincidentally functionalized by forming a catechol-Ti complex, as illustrated in Scheme 1. Furthermore, the cured films of sulfonated resins on the glass substrates exhibited improved hydrophilic behavior as expected. For example, 1SP-1T film showed a lower contact angle of 37° against water droplet, compared with the contact angle of 46° for unfunctionalized SiO₂-TiO₂.

The acid densities of the SiO₂-TiO₂-SO₃H specimens prepared at various compositions were determined with 0.01 M NaOH (aq), as summarized in Table 1. The acid density after the simple exchange of the Na⁺ ion of the SO₃Na moiety with a proton was approximately proportional to the extent of sulfonation, as shown in the elemental analysis (see ESI[†] Table S2). This may provide a protocol for introducing strong Brønsted acid sites to the surface. Alternatively, the acid strength was also measured using the Hammett indicators, anthraquinone and 2,4,6-trinitroaniline. The Hammett constants of binary SiO₂-TiO₂-SO₃H samples (1SP-4T) were in the range of -8.2 to -10.10, which were as acidic as nearly 90% sulfuric acid solution.⁹ However, the acid density of the hybrid 1HP-1T and 1HP-4T samples (see ESI[†] for notation) decreased drastically to 0.08 and 0.14 meq H⁺/g, respectively, presumably due to a blocking effect of the organic content on the active sites.

The solid acid catalytic performance of the SiO_2 -TiO₂-SO₃H mesoporous materials for esterification was evaluated with the condensation of acetic acid and ethanol at 80 °C using the powdery solid acids prepared in this study (Fig. 2).

The catalytic conversion was impressively high when compared to unfunctionalized SiO₂-TiO₂ and the background reaction with no catalyst. In particular, the initial reaction rates were considerably faster in nearly reaching completion in 60 min. In general, the conversion rate increased with increasing acid density, *i.e.*, the catecholic sulfonic acid content. The 1SP-4T with the highest acid density gave 73% and 99% yields in 10 min and 6 h, respectively. This



Fig. 2 Esterification of acetic acid and ethanol at 80 $^{\circ}$ C catalyzed by various SiO₂-TiO₂-SO₃H catalysts 0.1 g, acetic acid 17 mmol, ethanol 153 mmol: (a) 1SP-4T; (b) 1SP-1T; (c) 2SP-1T; (d) 1HP-4T; (e) 1HP-1T; (f) unfunctionalized SiO₂-TiO₂; (g) no catalyst.

Table 2 Esterification yields of 1SP-1T and 1SP-4T samples with
amount 0.1 g on various carboxylic acids at 80 $^{\circ}$ C^a

	Conversion, %						
Acid	1st use, 1 h	1st use, 6 h	2nd use, 6 h	3rd use, 6 h			
Acetic	61 (97)	97 (100)	85 (35)	70			
Propanoic	61 (80)	95 (98)	86 (39)	76			
Butanoic	55 (77)	94 (95)	87 (39)	78			
Lauric	26 (68)	92 (100)	88 (54)	86			
Palmitic	33 (66)	93 (100)	89 (55)	87			
Oleic	30 (60)	93 (100)	89 (55)	87			
a n .							

^{*a*} Reaction conditions: carboxylic acid = 17 mmol, EtOH = 153 mmol. 1SP-4T sample data, determined by GC, are shown in parentheses.

reveals that the catalytic activity of the developed SiO₂-TiO₂-SO₃H was higher than that of the reported SiO₂-SO₃H prepared by twostep sulfonation, 30% yield in 1 h and 90% 6 h.¹⁰ In the case of 1SP-4T and 1SP-1T, TOFs were higher than those of other catalysts owing to their relatively higher acidity and surface area. This remarkable acid catalytic activity of the newly developed solid acid, SiO₂-TiO₂-SO₃H, could be attributed to the enhanced acidic strength of the catecholic sulfonic acid due to the presence of a neighboring electron withdrawing phenyl group as well as the increased acid density inside the large pores by 2 acid groups in 1 molecule of catecholic acid.

The esterification of several organic acids with different chain lengths was also carried out. As shown in Table 2, the smaller the organic acid is, the faster it was converted because of the difference in mass transfer. Smaller molecules diffuse readily into the pores of mesoporous solid acids. The conversions of the larger fatty acids were generally lower than those of the smaller organic acids. But, the larger fatty acids also showed high conversion over 92% when the reaction time was extended to 6 h. The SiO2-TiO2-SO3H solid acids still exhibited higher catalytic activity for esterification than the other solid acids reported elsewhere.11 SBA-15-SO3H and HMS-SO3H with 2-3 nm pore showed the conversion of palmitic acid to the corresponding esters at 85% and 55%, respectively, at 85 °C for 3 h. Al-MCM-41 with a high surface area of 950-1023 m²/g showed 58% to 90% conversion of acetic acid at 100 and 200 °C in 8 h. MCM-41-SO₃H prepared by a two-step conventional process showed a 63% yield for the esterification of lauric acid at 112 °C in 8 h. It is believed that the large pores of this SiO2-TiO2-SO3H catalyst provide improved accessibility to large reactants, such as oleic acid and the ester by enabling the rapid diffusion of reactant and product through the pores, thereby minimizing consecutive reactions. Finally, it turned out that the activity of the solid acid catalyst decreases with repeated use. As shown in Table 2, the conversion of acetic acid by 1SP-1T decreased from 97% to 70% upon using it three times, each time

lasting 6 h, while the same conversion by 1SP-4T decreased to 35% from 100% upon using it two times, each lasting 6 h. The stability of 1SP-1T is comparable to that of the reported solid acid catalytic systems.^{1,2} It should be noted that the catalytic activity is better retained for larger fatty acids. This aspect of the catalyst that is related to the deactivation requires further study for definitive explanation of the behavior.

In summary, a simple one-step synthesis procedure for preparing a mesoporous SiO_2 -TiO_2-SO_3H solid acid catalyst has been presented, thereby providing a route to aromatic acid-functionalization with multiple acid sites. The solid acids have been shown to deliver a catalytic activity for esterification that is higher than those of the usual aliphatic sulfonic acid-functionalized ones and commercially available solid acid catalysts reported in the literature. This excellent catalytic performance could be attributed to the promoted acid strength of the sulfonic acid group in the presence of an electron withdrawing phenyl group, and the synergically large pore size. The SiO_2-TiO_2-SO_3H materials are useful as eco-friendly nanocatalysts for esterification and biofuel production.

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