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Design of Heterogeneous Catalysts via Multiple Active Site Positioning in Organic−Inorganic Hybrid Materials

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Abstract: Catalytic materials bearing multiple sulfonic acid functional groups and positioned at varying distances from one another on the surface of mesoporous solids are prepared to explore the effects that the spatial arrangement of active sites have on catalytic activity and selectivity. A series of organosiloxane precursors containing either disulfide or sulfonate ester functionalities (synthons of the eventual sulfonic acid groups) are synthesized. From these molecular precursors, a variety of organic−inorganic hybrid, mesostructured SBA-15 silica materials are prepared using a postsynthetic grafting procedure that leads to disulfide and sulfonate ester modified silicas: [Si]$CH_2CH_2CH_2SS$-pyridyl, **2**·SBA, [Si]$CH_2CH_2CH_2SSCH_2$-CH_2CH_2[Si], **3**·SBA, [Si]$CH_2CH_2(C_6H_4)(SO_2)OCH_2CH_3$, **4**·SBA, and [Si]$CH_2CH_2(C_6H_4)(SO_2)OC_6H_4O(SO_2)$-$(C_6H_4)CH_2CH_2$[Si], **6**·SBA ([Si] = ($\equiv$SiO)$_x$(RO)$_{3-x}$Si, where x = 1, 2). By subsequent chemical derivatization of the grafted species, thiol and sulfonic acid modified silicas are obtained. The materials are characterized by a variety of spectroscopic (^{13}C and ^{29}Si CP MAS NMR, X-ray diffraction) and quantitative (TGA/DTA, elemental analysis, acid capacity titration) techniques. In all cases, the organic fragment of the precursor molecule is grafted onto the solid without measurable decomposition, and the precursors are, in general, attached to the surface of the mesoporous oxide by multiple siloxane bridges. The disulfide species **2**·SBA and **3**·SBA are reduced to the corresponding thiols **7**·SBA and **8**·SBA, respectively, and **4**·SBA and **6**·SBA are transformed to the aryl sulfonic acids **11**·SBA and **12**·SBA, respectively. **7**·SBA and **8**·SBA differ only in terms of the level of control of the spatial arrangement of the thiol groups. Both **7**·SBA and **8**·SBA are further modified by oxidation with hydrogen peroxide to produce the alkyl sulfonic acid modified materials **9**·SBA and **10**·SBA, respectively. The performances of the sulfonic acid containing SBA-15 silica materials (with the exception of **12**·SBA) are tested as catalysts for the condensation reaction of phenol and acetone to bisphenol A. The alkyl sulfonic acid modified material **10**·SBA derived from the cleavage and oxidation of the dipropyl disulfide modified material **3**·SBA is more active than not only its monosite analogue **9**·SBA, but also the presumably stronger acid aryl sulfonic acid material **11**·SBA. It appears that a cooperative effect between two proximal functional groups may be operating in this reaction.

Introduction

An ongoing objective in the preparation of solid catalysts is the creation of structural uniformity. By analogy to soluble catalysts, structural homogeneity may lead to high selectivity. Clearly, results from zeolite-based catalysts suggest that there can be a strong correlation between mesoscopic/macroscopic uniformity and high selectivity.

A particularly attractive class of solids for investigating structure−property relationships are organic−inorganic hybrid materials.[1] One type of these hybrid solids utilizes inorganic materials to provide surface area and porosity and has organic functional groups attached to the surface. The organic groups can be randomly distributed or organized in some fashion, and are the active sites for catalytic reactions. Of current interest are (i) the creation of multiple organic groups in precise arrangements to study the effects of cooperativity, and (ii) the use of multiple organic group types to catalyze multistep reaction pathways.

Dual, organic functionalization of periodic, mesoporous silicas has been reported.[2−6] Typically, two types of organosilanes are used simultaneously to provide surface functionalized silicas. While one of the organic groups provides for the catalytic site, the other (may be alkyl, aryl, benzyl, or vinyl) normally is not another active site and is present to mediate the surface properties, for example, hydrophobicity. These methodologies do not provide for functional group positioning and control over uniformity.

Avnir and Blum have recently reported the use of multiple organic functionalities in accomplishing reaction networks within a single vessel.[7,8] Mutually destructive organic function-

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Scheme 1
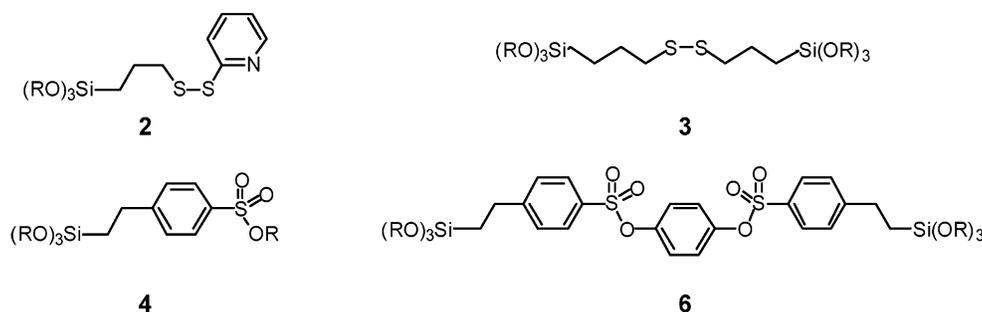
Scheme 2
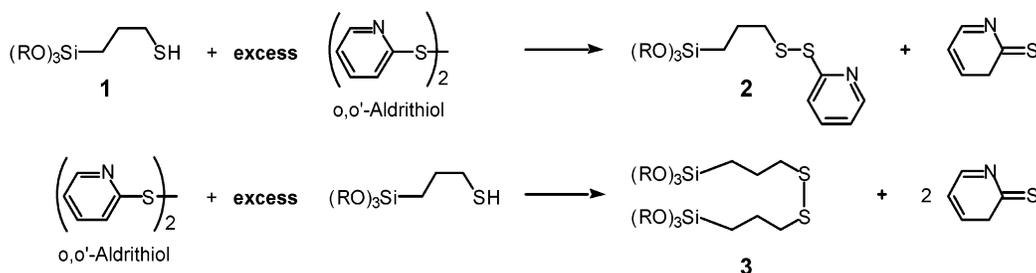
alities, for example, acids and bases, were entrapped separately in sol–gel-derived silicas and used together within a single reaction vessel to catalyze a sequence of reaction steps that in the absence of the "sol–gel protected" active centers would not proceed because of the annihilation of the active sites. Each solid contains a single type of organic group, and no method of control of functional group positioning was used.

Katz and Davis combined molecular imprinting with sol–gel synthesis techniques to prepare microporous, amorphous silicas with tailored microcavities containing multiple aminopropyl functional groups covalently attached to the silica.[9] The controlled positioning of two and three organic groups was accomplished, and the methodology has been extended to mesoporous materials.[10]

Here, we report on the synthesis and characterization of organic-functionalized, mesoporous silicas. The goal of our work is to develop methodologies to prepare uniform arrangements of organic functional groups on solid surfaces to access their ability to act in a cooperative fashion when accomplishing chemical reactions. Specifically, thiol and sulfonate ester functional groups were organized onto the ordered mesoporous solid SBA-15[11–14] through the use of designed organosilane coupling to surface silanol groups. The sulfur-containing moieties were converted to sulfonic acids, and the solids were tested as catalysts for the condensation reaction between acetone and phenol to produce bisphenol A. Particular attention was given to the characterization of the materials at each step of the preparation.

Results and Discussion

I. Synthesis of Molecular Precursors. A route to the preparation of mesoporous silica supported sulfonic acids involves the creation of a thiol containing silica, typically a mercaptopropyl functionalized silica, that is then oxidized, in a second step, with hydrogen peroxide.[15–18] A drawback of this approach when starting from a thiolsilane is the concurrent formation of disulfide groups that can produce a material that has various types of functional groups, notably partially oxidized

disulfides and other sulfur species.[15,18,19] To avoid these problems, we either protect the thiol functionality with a reversible blocking reagent such as a pyridyl group (precursor **2**) or use a sulfonate ester precursor (precursor **4**) to generate the sulfonic acid function.

To produce ordered, dimeric sites for comparison to the isolated sites that are generated from precursors **2** and **4**, precursors **3** and **6** were synthesized (Scheme 1). Starting from the symmetrical dipropyl disulfide (precursor **3**), two alkyl sulfonic acid groups in close proximity to one another may be produced by conversion to alkyl sulfonic acid centers, and from the molecular precursor bis(arylsulfonate ester) (precursor **6**), two aryl sulfonic acid sites can be generated by removal of the phenyl spacer.

Disulfide Microstructures (Unsymmetrical, 2; Symmetrical, 3). The unsymmetrical propylpyridyl disulfide **2** was obtained by reacting 3-mercaptopropyltrimethoxysilane, $(CH_3O)_3$-Si–$(CH_2)_3SH$, **1**, with 2,2′-dithiodipyridine (Aldrithiol) via a thiol–disulfide interchange reaction (Scheme 2).[20,21] If the thiol **1** is present in excess (2.5 equiv per disulfide bond), the product is the symmetrical dipropyl disulfide **3** (Scheme 2). After

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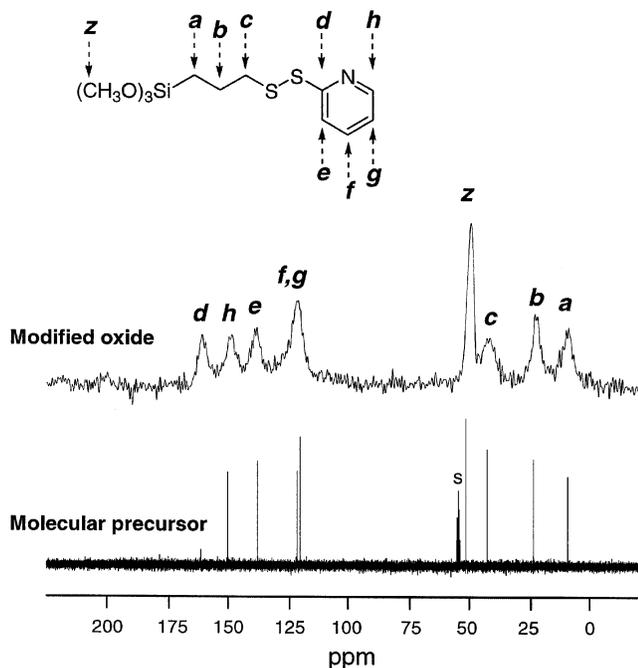(21) Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825–6836.

Figure 1. $^{13}C\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2; CP-MAS ^{13}C NMR spectrum of **2·SBA**. S denotes resonances from the solvent.
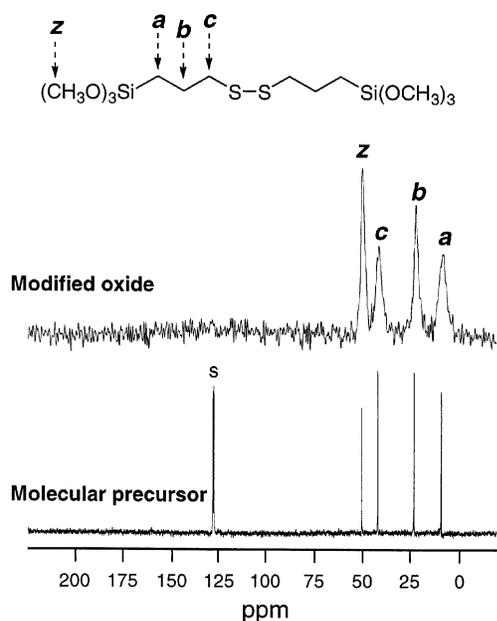

Figure 2. $^{13}C\{^1H\}$ NMR spectrum of **3** in C_6D_6; CP-MAS ^{13}C NMR spectrum of **3·SBA**. S denotes resonances from the solvent.

reaction (less than 3 h for **2**; 4 days to 1 week for **3**), both disulfide compounds are obtained in nearly quantitative yield by extraction with petroleum ether to remove the pyridine-2-thione.

Precursors **2** and **3** were characterized by ^1H and ^{13}C NMR spectroscopy and GC/MS in the case of **3**. The ^{13}C NMR spectra of both compounds (Figures 1 and 2 for **2** and **3**, respectively) exhibit in the 0−50 ppm region four signals: the resonances at around 40 and 22 ppm are attributed to the carbons of a propyl moiety situated, respectively, in α and β positions of the disulfide bond, the resonance at around 10 ppm to the carbon directly attached to the silicon atom, and the resonance at 48
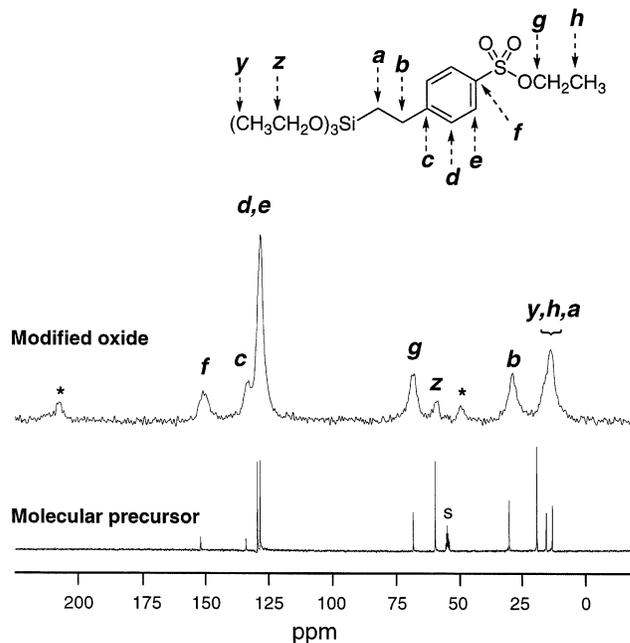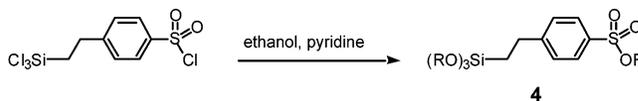

Figure 3. $^{13}C\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2; CP-MAS ^{13}C NMR spectrum of **4·SBA**. S denotes resonances from the solvent, and * marks spinning sidebands.

Scheme 3

ppm to the methoxy groups. In addition, downfield signals from all of the carbons of the pyridyl moiety are observed.

Monosulfonate Ester Microstructure, 4. The preparation of arylsulfonic acid esters was achieved by the reaction of an alcohol with the appropriate sulfonyl chloride in the presence of an organic base.[22] The sulfonyl chloride used here was the commercially available 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane), $(Cl)_3Si-(CH_2)_2-C_6H_4-SO_2Cl$. The reaction to the desired sulfonic acid ester was not clean.[23] Thus, the reaction of this chloride with ethanol in pyridine (Scheme 3) leads to precursor **4** in a relatively low yield (30%). Precursor **4** was characterized by ^1H and ^{13}C NMR. In particular, the ^{13}C NMR spectrum (Figure 3) exhibits two resonances at 14.8 and 67.3 ppm characteristic of the methyl and the methylene carbons of the ethylsulfonate group, respectively, and the signals of the ethoxysilane groups at 18.4 and 58.5 ppm. The alkyl carbon linked to the aromatic ring resonates at 29.4 ppm, while the carbon that attached to the silicon atom gives a chemical shift of 12.4 ppm. All of the resonances of the carbons of the aromatic ring are also observed in the 160−120 ppm region.

Disulfonate Ester Microstructure, 6. A two-step synthetic scheme was used to prepare **6** (Scheme 4). The first step involved the preparation of the aryl ester of *para*-vinylbenzenesulfonic acid by condensation of *para*-vinylbenzenesulfonic chloride with hydroquinone in the presence of pyridine to produce **5**, $CH_2=CH-C_6H_4-(SO_2)O-C_6H_4-O(SO_2)-C_6H_4-$

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(23) The starting 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane is sold as a solution in methylene chloride with 30% free sulfonic acid and small amounts of silylsulfonic acid condensation products. The sulfonic acid may react with EtOH to form diethyl ether and water, the latter inducing hydrolysis and condensation of the chlorosilane groups.

Scheme 4

6
+
isomers
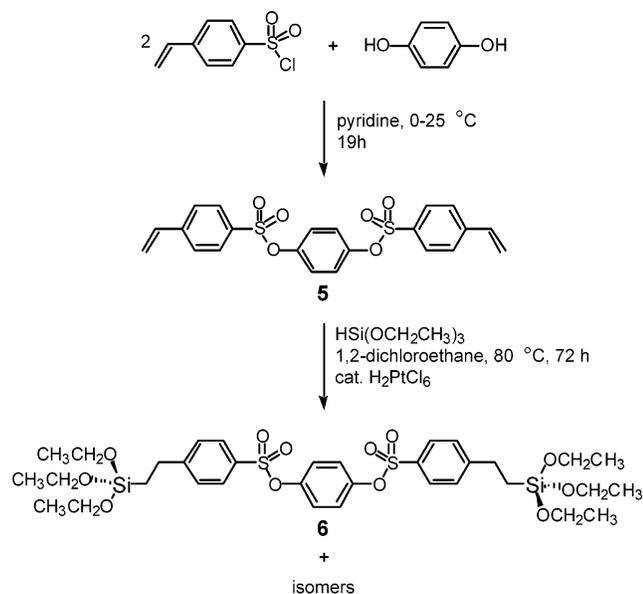
CH=CH$_2$, in 60% yield.[24] The vinyl groups of **5** were then hydrosilylated with triethoxysilane in the presence of chloroplatinic acid as the catalyst and 1,2-dichloroethane as the solvent.[25] Different hydrosilylation conditions were attempted,[26] but the best results were obtained when carrying out the reaction at 80 °C for several days and led to only 10% yield of the fully silylated product. The desired compound was a mixture of Markovnikov and anti-Markovnikov addition products, and this mixture is collectively referred to as **6** (Scheme 4 shows only the bis-anti-Markovnikov product). The complete silylation of both double bonds was evidenced by ^{1}H NMR spectroscopy, in particular, by the total disappearance of the signals at 5.4, 5.85, and 6.7 ppm typical of the carbons of the vinylic chain (see Supporting Information). The ^{13}C NMR spectrum of **6** is given in Figure 4.

II. Synthesis of Organic–Inorganic Hybrid Materials. Two major routes have been widely investigated to chemically modify the surface of periodic mesoporous silicas via covalently bound organic functionalities. The postsynthesis procedure involves the reaction of an organosilane directly with surface silanols of a surfactant-free mesoporous oxide and further modification or derivatization of the grafted species to create new functionalities.[27–30] The second approach, the so-called one-pot synthesis, combines the sol–gel[31] and supramolecular templating techniques to generate, in a single step, ordered organically modified mesoporous silica-based nanocomposites.[4,15,19,32–40] A number of groups report the synthesis of thiol and sulfonic acid modified ordered silicas by both the

grafting[17,41] and the co-condensation methods.[15,17,18,40,42] Most studies used the commercially available mercaptopropyltrimethoxysilane and, in a subsequent oxidation step, transformed the thiol to a sulfonic acid. Stucky and co-workers, however, report the addition of hydrogen peroxide with the mercaptopropyltrimethoxysilane or the 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane) in the reaction mixture to oxidize in situ the thiol functionalities.[4,40]

We have explored these different methods, but in this report we concentrate on the postsynthetic modification of the mesoporous silica and subsequent chemical modification of these surface functional groups. We will report results from the co-condensation synthesis strategy at a later time.

II. A. Grafting Reaction. SBA-15 type silicas were used as supports and were prepared by the acid catalyzed, nonionic assembly pathway described elsewhere.[11–14] The structure directing agent (Pluronic 123) was removed by calcination in air at 500 °C, and the organic-free mesoporous silica was rigorously dried under a flow of helium at 200 °C prior to the grafting reaction. The molecular precursors, **1**–**6**, were then reacted with the SBA-15 silica in toluene under reflux conditions. The unreacted precursors were removed by Soxhlet extraction with methylene chloride overnight, and the collected organic–inorganic hybrid materials are denoted **1·SBA**–**6·SBA**.

Quantitative determinations of the organic content of the hybrid mesoporous silicas were performed by thermogravimetric analysis (TGA) in air and by elemental analysis. The results are summarized in Table 1. The TGA data for several hybrid materials are given in the Supporting Information. Generally, three weight loss regions were observed. A first weight loss occurred at temperatures up to about 100 °C and was endothermic. This weight loss can be assigned to the desorption of water. A second weight loss followed at temperatures ranging from 150 to 650 °C, and this loss presumably arises from the decomposition of the organic and the desorption of its fragments (depending on the nature of the organic fragments, several desorption peaks could be observed in this region). The third significant weight loss peak occurred at temperatures above 650 °C and is due to the release of water formed from the condensation of silanols in the silica structure. For the purpose of reporting organic content in Table 1, the weight loss between 150 and 650 °C is taken as an estimate of the total amount of the organic. The functional group loadings for **1·SBA**–**6·SBA** are found to be 0.1–1.0 mmol/g of dry SiO$_2$ as determined by TGA and 0.2–0.9 mmol/g of dry SiO$_2$ as determined by sulfur analysis. The TGA data can overestimate the organic content because some weight loss below 650 °C can be due to silanol

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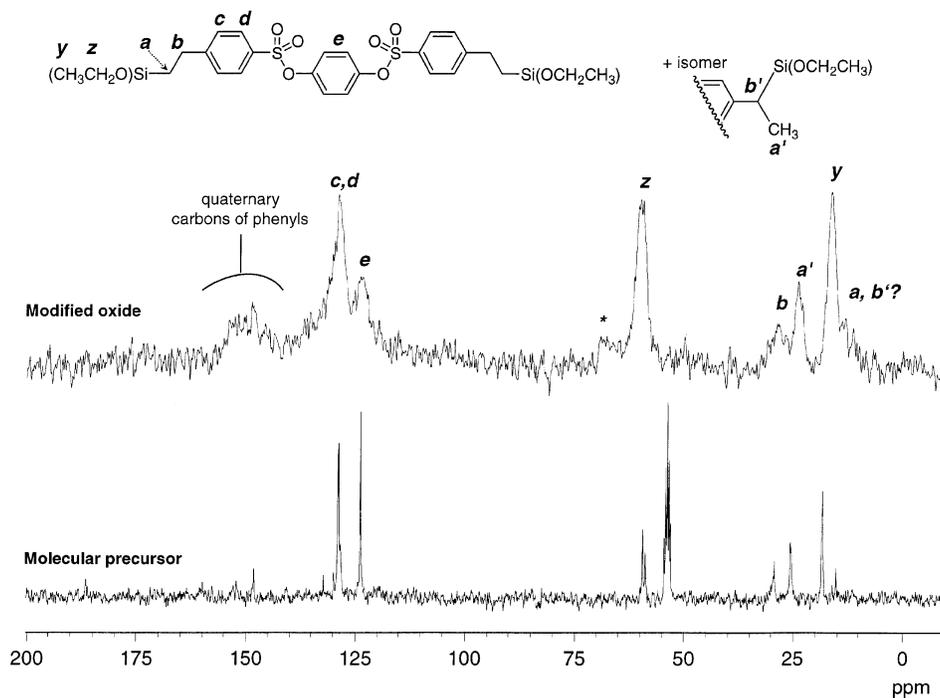
Figure 4. $^{13}C\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2; CP-MAS ^{13}C NMR spectrum of **6·SBA**.

Table 1. Organic and Acid Group Content of SBA-15 Type Silica Materials Containing Disulfide, Thiol, and Sulfonic Acid Fragments

			quantitative analysis of loading (mmol/g SiO_2)[a]			
sample	precursor	functional group	S wt %	derived from sulfur analysis	measured by TGA/DTA[b]	measured by acid capacity titration
1·SBA	**1**	[Si]−propyl−SH	1.4	0.47	0.6	n.d.[c]
2·SBA	**2**	[Si]−propyl−SS−pyridyl	4.1	0.79	0.87	n.d.
3·SBA	**3**	[Si]−propyl−SS−propyl−[Si]	3.3	0.62	0.85	n.d.
4·SBA	**4**	[Si]−CH_2CH_2aryl−SO_3Et	1.2	0.48	0.56	n.d.
6·SBA	**6**	[Si]−CH_2CH_2aryl−SO_3−aryl−SO_3−arylCH_2CH_2−[Si]	0.5	0.19	0.13	n.d.
7·SBA	**2**	[Si]−propyl−SH	2.0	0.71	1.3	n.d.
8·SBA	**3**	[Si]−propyl−SH HS−propyl−[Si]	2.7	0.93	0.80	n.d.
9·SBA	**2**	[Si]−propyl−SO_3H	1.4	0.54	0.66	0.33
10·SBA	**3**	[Si]−propyl−SO_3H HO_3S−propyl−[Si]	1.7	0.65	0.80	0.38
11·SBA	**4**	[Si]−CH_2CH_2aryl−SO_3H	0.76	0.29	0.47	0.26
12·SBA	**6**	[Si]−CH_2CH_2aryl−SO_3H HO_3S−arylCH_2CH_2−[Si]	<0.5	<0.2	0.40	0.035

[a] SiO_2 content in the solid derived from the value of dry mineral analyzed by TGA/DTA at 950 °C; mmol of organic functionality reported (e.g., in going from **3·SBA** to **8·SBA**, the value should double if there are no losses). [b] Weight loss of the organic moiety measured between 150 and 650 °C. [c] n.d. denotes not determined.

condensation that gives off water. Overall, the TGA data are in reasonable agreement with the elemental analysis results in most but not all cases.

Physicochemical (X-ray powder diffraction) and textural property (nitrogen sorption isotherms) data for the different hybrid materials are summarized in Table 2. X-ray diffraction patterns of the supported organic species exhibit three clear peaks in the 2θ-range of 0.6−3°, characteristic of hexagonally ordered mesophases with $d(100)$ spacing varying from 89 to 98 Å. The structure of the organic−inorganic hybrid materials is thus preserved throughout the grafting process. Nitrogen adsorption−desorption results from the organically modified SBA-15 silica materials show a type IV isotherm typical of mesoporous solids. A decrease in specific surface area between SBA-15 and the modified materials is observed and is attributable to the presence of the organic fragments.

The integrity of the organic fragment after grafting was confirmed by ^{13}C CP-MAS NMR spectroscopy. Figures 1−4 show the NMR spectra of the modified solids along with the solution phase spectra of the corresponding molecular precursors. Examination of Figures 1−4 leads to the conclusion that the organic functional groups remained intact during the grafting of the precursor and subsequent workup. Note that in the disulfide precursors **2** and **3**, the signal corresponding to the carbon atom adjacent to the thiol group (**c**) of precursor **1** (see Figure 5) has been shifted downfield to around 40 ppm, whereas the signal of the β-carbon has been shifted upfield to around 22 ppm. Corresponding peaks are resolvable in the CP-MAS NMR of the modified oxides. In Figure 3, it is not possible to resolve in the solid-state NMR spectrum the 10 signals that one might expect, but the peak at 67.3 ppm would indicate the presence of the sulfonate ester group (**g**). In Figure 4, the signals corresponding to the two types of phenyl moieties are well resolved; the central spacer is at 123 ppm, and the tether is at 128 ppm. For comparison to the materials prepared from precursors **2**−**6**, **1** was grafted onto SBA-15, and the ^{13}C NMR spectrum from the material obtained is given in Figure 5.

Table 2. Physical and Textural Properties of SBA-15 Type Silica Materials Containing Disulfide, Thiol, and Sulfonic Acid Fragments
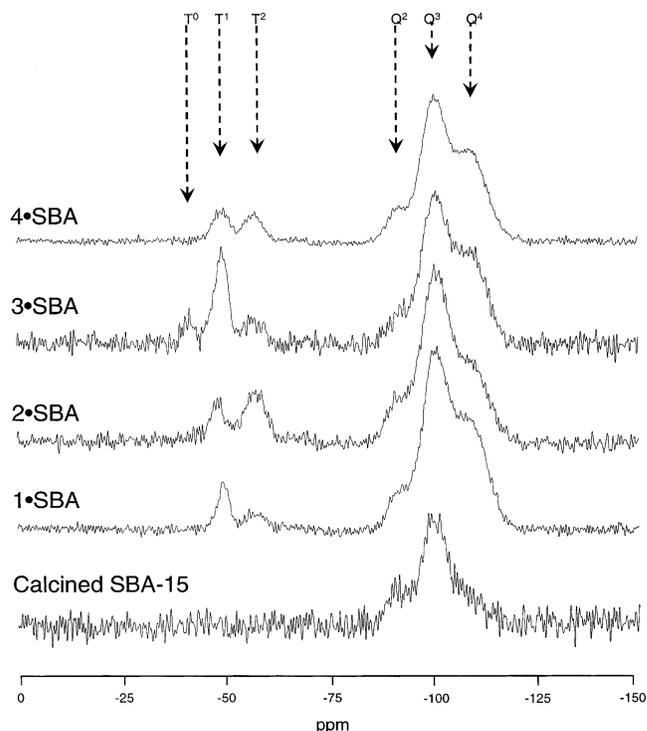
sample	precursor	functional group	XRD		textural properties	
			$d_{100}{}^a$ (Å)	wall thickness^b (Å)	$D_p{}^c$ (Å)	S_{BET} (m^2 g^{-1})
SBA-15			105	41.2	80	806
2·SBA	**2**	[Si]−propyl−SS−pyridyl	93	51.4	56	545
3·SBA	**3**	[Si]−propyl−SS−propyl−[Si]	89	48.8	54	580
4·SBA	**4**	[Si]−CH$_2$CH$_2$aryl−SO$_3$Et	89	43.8	59	647
6·SBA	**6**	[Si]−CH$_2$CH$_2$aryl−SO$_3$−aryl−SO$_3$−arylCH$_2$CH$_2$−[Si]	98	53.2	60	765
7·SBA	**2**	[Si]−propyl−SH	103	60.9	58	669
8·SBA	**3**	[Si]−propyl−SH HS−propyl−[Si]	96	56.8	54	656
9·SBA	**2**	[Si]−propyl−SO$_3$H	n.d.^{d}	n.d.	60	619
10·SBA	**3**	[Si]−propyl−SO$_3$H HO$_3$S−propyl−[Si]	n.d.	n.d.	55	520
11·SBA	**4**	[Si]−CH$_2$CH$_2$aryl−SO$_3$H	100	54.5	61	697

^{a} $d(100)$ spacing. ^{b} Calculated by $(a_0 -$ pore size) with $a_0 = 2d_{100}/\sqrt{3}$. ^{c} Pore size from desorption branch using the BJH method of analysis. ^{d} n.d. denotes not determined.
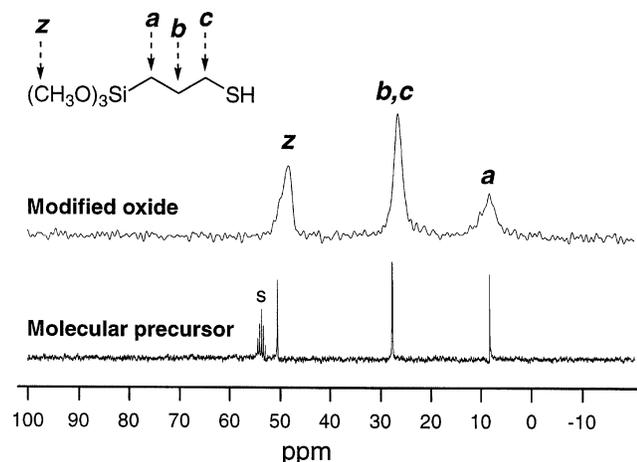
Figure 5. ^{13}C{^{1}H} NMR spectrum of **1** in CD$_2$Cl$_2$; CP-MAS ^{13}C NMR spectrum of **1**·SBA. S denotes resonances from the solvent.

The ^{29}Si CP-MAS NMR spectra of the modified oxides, **1**·SBA−**4**·SBA, are presented together with the nonmodified silica support SBA-15 in Figure 6. The peaks observed in the spectral region associated with tertiary silicon atoms, from −40 to −75 ppm, indicate unambiguously the presence of organosiloxane moieties.[43] Furthermore, multiple peaks are obtained from each of the modified oxides, suggesting different degrees of linkage of the organosiloxane group with the silica surface. All four modified oxides exhibit principally T^1 and T^2 sites, that is, an anchoring of the organic species via one or two Si−O−Si bonds. It is important that only the oxide modified by the dipropyl disulfide, **3**·SBA, exhibits a signal at −41 ppm corresponding to a T^0 site. This precursor is unique in that it contains two polymerizable alkoxysilane moieties and perhaps, in the context of a postsynthetic grafting procedure, it is impossible to find sufficient available surface silanols for further condensation. Peaks assignable to Q^2, Q^3, and Q^4 silicon sites are discernible in all five spectra.

II. B. Chemical Modification of the Grafted Species. Thiol Site Generation by Cleavage of Disulfide Linkages. Organophosphines have been used as reducing agents to cleave S−S bonds.[44−46] The reductions of **2**·SBA and **3**·SBA were carried

(43) The conventional notation for the silicon atom type is used. A capital letter Q or T indicates the type of silicon atom, Q or quaternary having four Si−O bonds as in a siloxane, and T tertiary having three Si−O bonds, as in an organosiloxane. The capital letter is followed by the number of Si−O−Si bonds attached to the center. Thus, the central silicon atom of RSi(OSi)(OR′)$_2$ is T^1, of RSi(OSi)$_2$(OR′) is T^2, and of RSi(OSi)$_3$ is T^3.
(44) Kirley, T. L. *Anal. Biochem.* **1989**, *180*, 231−236.
(45) Ruegg, U. T.; Rudinger, J. *Methods Enzymol.* **1977**, *47*, 111−126.

Figure 6. CP-MAS ^{29}Si NMR spectra of calcined SBA-15, **1**·SBA, **2**·SBA, **3**·SBA, and **4**·SBA.

out at 55 °C in the presence of a slight excess of tris(2-carboxyethyl)-phosphine TCEP·HCl (2 equiv per disulfide unit)[46] and were monitored by CP-MAS ^{13}C NMR spectroscopy. In the case of the reduction of the pyridyl-propyl disulfide linkage of **2**·SBA to produce the surface thiol **7**·SBA, the ^{13}C NMR spectrum (Figure 7) showed the total disappearance of the resonances at 40 and 23 ppm characteristic of the carbons of the propyl chain situated, respectively, in α and β positions from the disulfide bond as well as those in the 160−115 ppm region corresponding to the carbons of the pyridyl group. Simultaneously, a new resonance at 27.5 ppm appeared that can be assigned to the adjacent and central methylene carbons of a propylthiol moiety (by analogy to the ^{13}C NMR of **1**·SBA that was synthesized directly). Taken together, these observations indicate quantitative cleavage of all of the disulfide bonds present in the material to yield clean disulfide-free mercapto-propyl functionalities. Also, the clean conversion of the dimeric

(46) Burns, J. A.; Butler, J. C.; Moran, J.; Whitesides, G. M. *J. Org. Chem.* **1991**, *56*, 2648−2650.
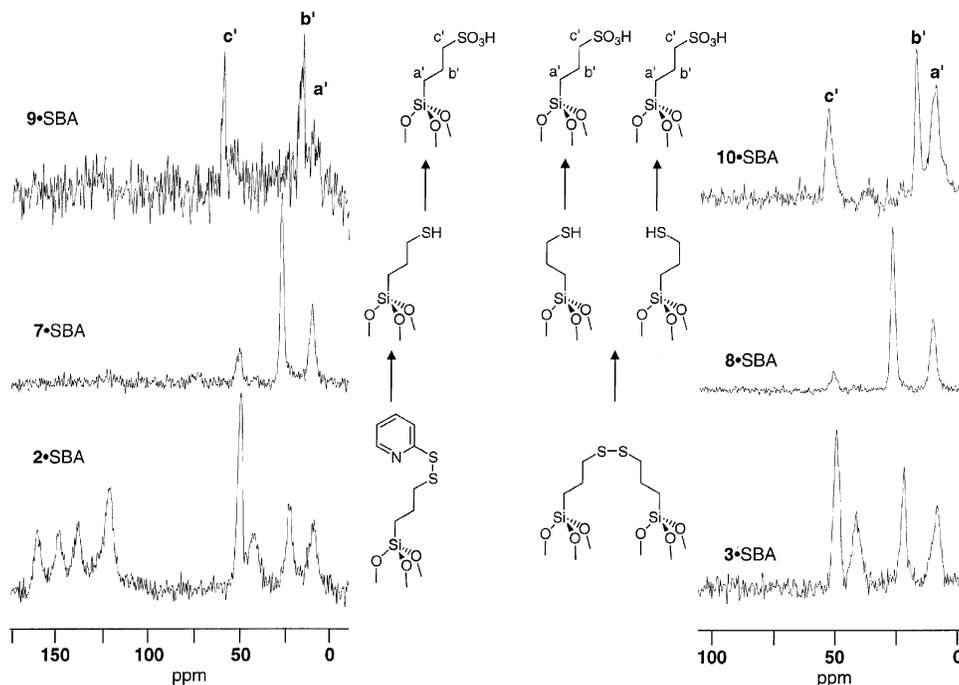
Figure 7. CP-MAS ^{13}C NMR spectra of (left) **2·SBA**, **7·SBA**, and **9·SBA**; (right) **3·SBA**, **8·SBA**, and **10·SBA**, corresponding to the subsequent disulfide cleavage and oxidation reaction.

disulfide, **3·SBA**, to an analogous mercaptopropyl containing material, **8·SBA**, is observed. Note that **8·SBA** differs from **7·SBA** in that the mercaptopropyl moieties are placed in pairs on the surface of the mesoporous silica. Another effect of the transformation of **2·SBA** and **3·SBA** is the significant decrease of the intensity of the signal at 48 ppm corresponding to methoxy groups. The ^{29}Si CP-MAS NMR spectra of the materials after this transformation (see Supporting Information) show significant decreases of T^1 signals and increases in the T^2 and T^3 signals. Thus, the reduction conditions appear to facilitate further reaction between unreacted SiOCH$_3$ of the organosiloxane and the silica surface.

The surface area measurements show for both materials that the reduction of the disulfide linkage is accompanied by an increase in the specific surface area (Table 2). The powder X-ray diffraction patterns of these solids still indicate the hexagonal ordering (Table 2 and Supporting Information).

Sulfonic Acid Active Site Generation. Two methods were used to produce the desired catalytically active sulfonic acid surface functional groups. A procedure commonly employed is the mild oxidation of thiol surface functional groups by H$_2$O$_2$,[15–18] and this method was applied to **7·SBA** and **8·SBA**. A second method used here involved the hydrolysis of sulfonate ester surface functional groups and was exploited with **4·SBA** and **6·SBA**.

Oxidation of the Surface Thiol Functional Groups. The oxidation of the mercaptopropyl groups was performed using the procedure described by Margolese et al.[4] In a typical reaction, 300 mg of the thiol containing material was suspended in aqueous H$_2$O$_2$, and the suspension was stirred at room temperature overnight under an atmosphere of argon. The solid was filtered, acidified with sulfuric acid, washed, and finally dried at 80 °C overnight (**9·SBA** and **10·SBA**).

The ^{13}C CP-MAS NMR spectra of **9·SBA** and **10·SBA** (Figure 7) show the complete disappearance of the signal at

27.5 ppm, characteristic of the carbon directly linked to the thiol functional group, and the appearance of new peaks at 18 and 54 ppm, typical of *n*-alkyl sulfonic acids.[47] Weak signals at 22, 39, and 64 ppm can also be seen in the spectra from **9·SBA** and **10·SBA**. These resonances have been observed previously for this type of oxidation and have been attributed to disulfide and partially oxidized disulfide species.[15,19] The formation of nonacidic sulfur containing side products could explain the difference between sulfur loading and the acid capacity titration for these materials reported in Table 1 (0.54 mmol/g SiO$_2$ vs 0.33 mmol/g SiO$_2$ for **9·SBA**, 0.65 mmol/g SiO$_2$ vs 0.38 mmol/g SiO$_2$ for **10·SBA**). Also, it is noted that some organic is lost from the treatments with H$_2$O$_2$ (**7·SBA** vs **9·SBA**; **8·SBA** vs **10·SBA**).

The oxidation of thiol to sulfonic acid is accompanied by a decrease in the specific surface area from the value obtained after reduction, and this effect has also been reported by other authors.[4,15,19] The X-ray powder diffraction patterns exhibit three clear peaks, indicating that the hexagonal ordering of the material is maintained.

Sulfonate Ester Transformation. The sulfonate ester moieties in **4·SBA** and **6·SBA** were hydrolyzed in an aqueous solution of sulfuric acid at 60 °C overnight.[48] The solids were filtered, washed, and dried at 80 °C.

For **4·SBA**, ^{13}C CP-MAS NMR (see Supporting Information) confirmed the complete transformation of ethyl sulfonate to sulfonic acid as was evidenced by the total disappearance of the peak at 67.3 ppm attributed to the methylene carbons of that group. Also, the resonance at 58 ppm attributed to the ethoxysilane fragment disappears. These data compare favorably with those reported by Melero et al. for arenesulfonic modified

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(47) The chemical shifts are consistent with those calculated for molecular alkylsulfonic acid, for example, 1-propane sulfonic acid.
(48) Bentley, T. W.; Jurczyk, S.; Roberts, K.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 293–300.

Scheme 5

p,p'-bisphenol-A   o,p'-bisphenol-A
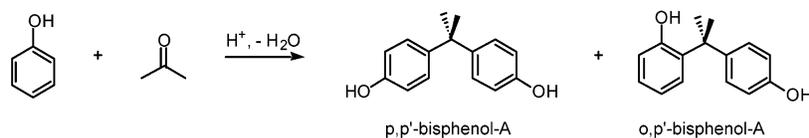
Table 3. Synthesis of Bisphenol A with Sulfonic Acid Functionalized SBA-15 Silicas and *para*-Toluene Sulfonic Acid[a]

catalyst	functional group	per site yield of bisphenol A[b]		p, p'/o, p' molar ratio	
		GC[c]	NMR[d]	GC[c]	NMR[d]
para-toluene sulfonic acid	CH₃aryl−SO₃H	36	29	2	2.6
1-propane sulfonic acid	CH₃CH₂CH₂−SO₃H	9.6[e]	n.d.[f]	1.8[e]	n.d.
11·SBA	[Si]−CH₂CH₂aryl−SO₃H	13	11	3	3.0
9·SBA	[Si]−propyl−SO₃H	8.8	8.4	10	6.4
10·SBA	[Si]−propyl−SO₃H HO₃S−propyl−[Si]	18	18	12	8.3

[a] Reagents and conditions: phenol/acetone molar ratio = 7/1; acetone/−SO₃H site = 300; 85 °C, 24 h. [b] mol of bisphenol A/mol of active site. [c] Analysis performed using biphenyl as external standard in acetonitrile. [d] Analysis performed using mesitylene as external integration standard in CD₃OD. [e] Analysis performed using liquid chromatography. [f] n.d. denotes not determined.

SBA-15 materials obtained by co-condensation of 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane) and TEOS in the absence and presence of H₂O₂.[40] The acid capacity via titration methods indicates the presence of acidic functional groups (presumably arylsulfonic acid groups) with a loading very similar to the sulfur loading as measured by elemental analysis (0.29 mmol/g SiO₂ vs 0.26 mm/g SiO₂, respectively, Table 1).

For **6·SBA**, the ¹³C CP-MAS NMR spectrum was of poor quality (likely due to low organic loading), but the total disappearance of the signal at 123 ppm characteristic of the phenyl spacer of **6** was observed. The acid capacity measurement showed very little sulfonic acid. Because of these low values, we did not use this material for the catalytic reaction studies.

III. Catalysis. Sulfonic acid functionalized mesoporous materials have been synthesized and successfully tested in a large number of acid-catalyzed reactions such as condensation or esterification reactions.[17,19,40,49,50] To evaluate the catalytic performances of the aryl and alkyl sulfonic acid containing SBA-15 silicas and to address the question of whether the spatial arrangement of the active sites is of importance, the condensation of phenol and acetone to produce bisphenol A (Scheme 5) was investigated. Bisphenol A is an important raw material for resin and polymer production. It is conventionally manufactured by condensation of phenol and acetone catalyzed by ion-exchange resins.[51] However, because the thermal stability of resins can be limited, the search for alternative, thermally stable, solid acids continues. The use of heteropolyacid compounds supported on MCM-41 type silicas or clays as well as zeolites such as H-ZSM-5 and H-Y, and the use of silica supported sulfonic acids have been reported.[51−55]

The catalytic activity and selectivity of **9·SBA**, **10·SBA**, and **11·SBA** and the homogeneous catalysts 1-propane sulfonic acid and *para*-toluene sulfonic acid were tested at the same reaction conditions (see below). The **9·SBA** and **11·SBA** solids are used to compare heterogeneous analogues to their homogeneous

counterparts. Results from **9·SBA** and **11·SBA** provide a comparison between alkyl and aryl sulfonic acid modified mesoporous silica materials. Finally, the effects of dimeric sites in **10·SBA** are compared to the individual sites of **9·SBA** to probe the importance of positioning of the catalytic groups.

The batch, condensation reaction was carried out in the absence of solvent in a sealed glass vessel at 85 °C for 24 h. Phenol was in excess (7 mol per mol of acetone), and the acetone/acid active site molar ratio was fixed at 300. At the end of the reaction period, a sample was analyzed by gas chromatography with the addition of a known amount of an external standard. An independent sample was analyzed by ¹H NMR with an external proton integration standard. The results of the two methods were consistent and are reported in Table 3.

At these reaction conditions, the two structural isomers of bisphenol A were formed with all of the catalysts studied (see Scheme 5). The "per site yield" listed in Table 3 represents the total molar quantity of the two isomers divided by the total molar equivalents of acid as determined (in the case of solid acids) by titration.

para-Toluene sulfonic acid is the most active catalyst studied. The regioselectivity of the condensation vis-à-vis the phenol group is as expected, that is, predominantly para-activation with respect to the hydroxyl group with some ortho-activated side product. The solid aryl sulfonic acid catalyst, **11·SBA**, is about one-third less active than the homogeneous system at roughly the same selectivity.

9·SBA exhibited a lower activity than **11·SBA**, as might be expected given the lower acid strength of the alkyl sulfonic acid as compared to the aryl sulfonic acid.[40] However, the change in the regioselectivity of the reaction is unexpected. The ratio of *p,p'*-bisphenol A to *o,p'*-bisphenol A is much higher for the propylsulfonic acid modified SBA-15, **9·SBA**, than the aryl sulfonic acid modified SBA-15, **11·SBA** (10 vs 3). Additionally, the regioselectivity of **9·SBA** is high as compared to the analogous homogeneous catalyst (1-propane sulfonic acid) at an equivalent reaction rate. Because the regioselectivity of the heterogeneous catalyst is so different from that of the homogeneous catalyst, leaching from the solid must not occur to any significant extent. However, to test further for any indications of leaching, **9·SBA** was filtered from a solution that was reacted

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(51) Yadov, G. D.; Kirthivasan, N. *Appl. Catal., A* **1997**, *154*, 29−53.
(52) Singh, A. P. *Catal. Lett.* **1992**, *16*, 431−435.
(53) Nowinska, K.; Kaleta, W. *Appl. Catal., A* **2000**, *203*, 91−100.
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(55) Wieland, S.; Panster, P. *Stud. Surf. Sci. Catal.* **1997**, *108*, 67−74.

for 24 h. The filtrate was then reacted for an additional 24 h at 85 °C (absence of solid), and no further conversion was observed.

The catalyst produced by placing two organic functionalities in close proximity on the silica surface, **10·SBA**, exhibited not only the highest activity of the heterogeneous systems but also the highest regioselectivity of all of the systems considered here. The principal difference in the performance related to spatial arrangement of the functional groups, that is, between **9·SBA** and **10·SBA**, is of activity rather than regioselectivity, as the per site yield is practically doubled by having pairs of alkyl sulfonic acid groups (18 vs 8.8 by GC). Additionally, **10·SBA** is even more active than 1-propane sulfonic acid (18 vs 9.6). While there must be some cooperative effect occurring, the exact nature of this effect cannot be conclusively obtained from the data presented here.

A number of groups have disclosed the utility of using mixed thiol/sulfonic acid catalytic systems to enhance activity and selectivity.[55-58] However, Cheng and co-workers reported recently that catalysts containing incompletely oxidized sulfur species exhibited lower catalytic activity.[54] From the data given in Table 1, the acid capacity of the propylsulfonic acid modified materials is always less than the sulfur elemental analyses, and this could indicate the presence of nonsulfonic acid sites on the surface. It may be that these sites are playing a role in the catalysis and that the enhancement observed between **9·SBA** and **10·SBA** could be due to the systematic proximity of the sulfonic acid sites and the nonsulfonic acid sites. However, the current level of characterization of these materials does not allow us to confidently test this hypothesis. Alternatively, the enhancement of activity may be due to cooperation between two proximal sulfonic acid groups on the surface, and the nonacidic sites may not participate at all.

Among our future studies, we are most interested in testing these various hypotheses. The synthesis of large quantities of clean diacid materials such as **12·SBA** and of materials derived from molecular precursors having both thiol and acid functional synthons should provide quantitative formation of sulfonic acid dimer sites (like that obtained with **11·SBA** for monomeric sites − Table 1) and sites containing a single sulfonic acid and a single thiol to give clearer evidence for any cooperative effects.

Experimental Section

All manipulations were conducted under a strict inert atmosphere or vacuum conditions using Schlenk techniques. The solvents (CH₂-Cl₂, petroleum ether, and toluene) were dried by passing them through a drying column and stored over activated 4 Å molecular sieves.

2,2′-Dithiodipyridine (Aldrithiol), tetraethoxysilane (TEOS), and poly(ethyleneoxide)−poly(propyleneoxide)−poly(ethyleneoxide) block copolymer (Pluronic 123, mw: 5000) were purchased from Aldrich Chemical and used without further purification. 3-Mercaptopropyltri-methoxysilane and 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane), 50% in methylene chloride, were obtained from Gelest. Tris(2-carboxyethyl)-phosphine (TCEP·HCl) was purchased from Pierce.

Synthesis Procedure. A. Preparation of Molecular Precursors. Synthesis of (CH₃O)₃Si−(CH₂)₃−SS−C₅H₅N, 2. A solution of **1** (1 g, 5.1 mmol) in dry CH₂Cl₂ (5 mL) was added dropwise at room temperature over a period of 2 h to a solution of 2,2′-dithiodipyridine

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(3.36 g, 15.3 mmol) in CH₂Cl₂ (20 mL). The initially colorless solution turned yellow immediately after the addition of **1** due to the production of pyridine-2-thione. After the complete addition of **1**, the solution was stirred an additional hour, and the solvent was removed in vacuo. The unsymmetrical disulfide was then extracted with dry petroleum ether, filtered, and dried under vacuum. Precursor **2** was obtained in 95% yield as a moisture-sensitive yellow liquid.

For **2**: ¹H NMR, CD₂Cl₂, δ 0.71 ppm (m, 2H, SiCH₂CH₂CH₂SS), 1.77 ppm (quintet, 2H, SiCH₂CH₂CH₂SS, ³J$_{HH}$ = 7.13 Hz), 2.8 ppm (t, 2H, SiCH₂CH₂CH₂SS, ³J$_{HH}$ = 7.5 Hz), 3.48 ppm (s, 3H, OCH₃), 7.06, 7.67, 7.73, and 8.42 ppm (m, 5H of the pyridyl group); ¹³C{¹H} NMR, CD₂Cl₂, δ 8.8 ppm (SiCH₂CH₂CHSS), 22.9 ppm (SiCH₂CH₂-CH₂SS), 42.1 ppm (SiCH₂CH₂CH₂SS), 50.8 ppm (s, OCH₃), 119.7, 120.9, 137.4, 149.9, and 161.1 ppm (pyridyl carbons).

Synthesis of [(CH₃O)₃Si−(CH₂)₃−S−]₂, 3. An excess of 3-mer-captopropyltrimethoxysilane (4.45 g, 22.6 mmol) was added rapidly via a syringe to a solution of 2,2′-dithiodipyridine (2 g, 9.07 mmol) in CH₂Cl₂ (20 mL), and the yellow solution was stirred at room temperature during 4 days. Precursor **3** was then purified by extraction with petroleum ether as described above. The reaction yielded **3** quantitatively as a yellow liquid.

For **3**: ¹H NMR, CD₂Cl₂, δ 0.66 ppm (m, 2H, SiCH₂CH₂CH₂SS), 1.85 ppm (quintet, 2H, SiCH₂CH₂CH₂SS, ³J$_{HH}$ = 7.2 Hz), 2.52 ppm (t, 2H, SiCH₂CH₂CH₂SS, ³J$_{HH}$ = 7.2 Hz), 3.46 ppm (s, 3H, −OCH₃); ¹³C{¹H} NMR, CD₂Cl₂, δ 8.7 ppm (SiCH₂CH₂CH₂SS), 22.9 ppm (SiCH₂CH₂CH₂SS), 42.8 ppm (SiCH₂CH₂CH₂SS), 50.2 ppm (−OCH₃). GC-MS: 390 (M⁺), 196 (M⁺ − (CH₃O)₃Si−(CH₂)₃−S−), 163 ((CH₃O)₃Si−(CH₂)₃− fragment), 121 ((CH₃O)₃Si− fragment).

Synthesis of (EtO)₃Si(CH₂)₂C₆H₄−SO₂OEt (with Et = −CH₂CH₃), 4. 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane) (8 mL of a 50% methylene chloride solution, 16.2 mmol) was added dropwise through a septum to a solution of dry ethanol (9.44 mL, 162 mmol) and pyridine (30 mL) at 0 °C. After the addition, the solution was kept at 0 °C an additional 2 h, and the mixture was allowed slowly to warm at room temperature. The reaction mixture was stirred at 25 °C overnight, and, after the removal of pyridine under vacuum, **4** was extracted with petroleum ether (30% yield).

For **4**: ¹H NMR, CD₂Cl₂, δ 1 ppm (m, 2H, SiCH₂CH₂), 1.22 ppm (t, 3H, SiOCH₂CH₃, ³J$_{HH}$ = 7.2 Hz), 1.3 ppm (t, 3H, SO₂OCH₂CH₃, ³J$_{HH}$ = 7.2 Hz), 2.82 ppm (m, 2H, SiCH₂CH₂), 3.82 ppm (quadruplet, 2H, SiOCH₂CH₃, ³J$_{HH}$ = 6.5 Hz), 4.08 ppm (quadruplet, 2H, SO₂OCH₂-CH₃, ³J$_{HH}$ = 7.2 Hz), 7.42 ppm (d, 2H, phenyl protons situated in β of the ethyl chain, ³J$_{HH}$ = 8.3 Hz), 7.80 ppm (doublet, 2H, phenyl protons situated in β of the sulfonate ester group, ³J$_{HH}$ = 8.2 Hz); ¹³C{¹H} NMR, CD₂Cl₂, δ 12.4 ppm (SiCH₂CH₂), 14.8 ppm (SO₂OCH₂CH₃), 18.4 ppm (SiOCH₂CH₃), 29.4 ppm (SiCH₂CH₂), 58.5 ppm (SiOCH₂-CH₃), 67.3 ppm (SO₂OCH₂CH₃), 128 and 128.9 ppm (carbons of the aromatic ring), 133 ppm (quaternary carbon of the aromatic ring attached to the ethyl chain), 152 ppm (ipso carbon attached to the ethyl sulfonate group).

Synthesis of (EtO)₃Si(CH₂)₂−C₆H₄−(SO₂)O−C₆H₄−O(SO₂)−C₆H₄−(CH₂)₂Si(OEt)₃, 6. The synthesis of **6** was achieved in two steps: esterification of the *para*-styrene sulfonyl chloride with hydro-quinone in the presence of pyridine leading to the formation of a diolefinic compound containing two sulfonate ester moieties, CH₂= CH−C₆H₄−(SO₂)O−C₆H₄−O(SO₂)−C₆H₄−CH=CH₂, **5**, and hydrosi-lylation of the two double bonds in **5** with triethoxysilane in the presence of chloroplatinic acid as the catalyst to yield **6**.

(a) Preparation of CH₂=CH−C₆H₄−(SO₂)O−C₆H₄−O(SO₂)−C₆H₄−CH=CH₂, 5. Hydroquinone (0.7 g, 6.35 mmol) was dissolved in dry pyridine (20 mL), and the solution was cooled to 0 °C 1 h prior to the addition of the *para*-styrene sulfonyl chloride (2083 g, 14 mmol), introduced via a syringe under an argon atmosphere. The mixture kept at 0 °C an additional 2 h was allowed to warm to room temperature and left overnight. The reaction was quenched with an acidified aqueous solution (75 g of crushed ice and 25 mL of concentrated hydrochloric

acid), and the solution was diluted with methylene chloride. The organic layer was first neutralized by successive washings with sodium bicarbonate solution and then washed with a brine solution. The combined organic extracts were then dried over magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure. Finally, **5** was recrystallized from the resultant white powder with a mixture of $HCCl_3$ and petroleum ether and was obtained in 60% yield.

For **5**: ^{1}H NMR, CD_2Cl_2, δ 5.42 ppm (d, 1H, arylCH=CH_2, $^{cis}J =$ 11 Hz), 5.85 ppm (d, 1H, arylCH=CH_2, $^{trans}J = 18$ Hz), 6.7 ppm (complex multiplet, 1H, arylCH=CH_2, $^3J_{HH} = 10.9$ and 17.6 Hz), 6.84 ppm (s, 4H, protons of the central phenyl moiety), 7.45 ppm (d, 2H, aryl protons, $^3J_{HH} = 8.4$ Hz), 7.62 ppm (d, 2H, aryl protons, $^3J_{HH} = 8$ Hz); ^{13}C{^{1}H} NMR, CD_2Cl_2, δ 118.6 ppm (Aryl$-CH$=CH_2), 123.8 ppm ($-CH$ of the central phenyl ring), 127 and 129 ppm ($-CH$ of the aromatic ring), 133.5 ppm (quaternary carbons of the central phenyl ring), 135.1 ppm ($-CH$=CH_2), 143.8 ppm (quaternary carbon of the aromatic ring attached to the vinyl chain), 148.1 ppm (quaternary carbon of the aromatic ring attached to the sulfonate ester group).

(b) Preparation of $(EtO)_3Si(CH_2)_2-C_6H_4-(SO_2)O-C_6H_4-O(SO_2)-C_6H_4-(CH_2)_2Si(OEt)_3$ **and Related Isomers Referred to as 6.** The addition of triethoxysilane, $HSi(OEt)_3$, in the presence of chloroplatinic acid, to the di-olefinic compound **5** produced **6** as a mixture of anti-Markovnikov and Markovnikov addition products. Typically, 1 g of **5** (22.62 mmol) was first dissolved in the minimum amount of 1,2-dichloroethane (1 mL), and 5 mg of $H_2PtCl_6\cdot6H_2O$ (0.0122 mmol) was then added to the solution. Triethoxysilane (0.82 g, 5 mmol) was added dropwise to this mixture at 80 °C over 15 min. After 4 days of reaction at the same temperature, the fully silylated products were purified by extraction with petroleum ether.

For **6**: ^{1}H NMR, CD_2Cl_2, δ 0.86 ppm (m, 2H, SiCH_2CH_2), 1.12 ppm (m, Si$-OCH_2CH_3$ and CH(Si)$-CH_3$), 2.66 ppm (quadruplet, 1H, $-CH$(Si)$-CH_3$, $^3J_{HH} = 7.6$ Hz), 2.71 ppm (m, 2H, SiCH_2CH_2), 3.73 ppm (m, Si$-OCH_2CH_3$), 6.82 ppm (s, 4H, aryl protons of the central phenyl moiety), 7.3 and 7.6 ppm (two doublets, 4H, aryl protons, $^3J_{HH} = 8.8$ and 7.6 Hz, respectively); ^{13}C{^{1}H} NMR, CD_2Cl_2, δ 15.1 and 16 ppm ($-CH$ and $-CH_2$, carbons directly attached to a silicon atom), 18.2 ppm (Si$-OCH_2CH_3$), 25.4 and 25.6 ppm (CH(Si)$-CH_3$), 29.2 ppm (SiCH_2CH_2), 58.7 and 59.3 ppm (Si$-OCH_2CH_3$), 123.7 ppm ($-CH$ of the central phenyl ring), 128.6 and 128.8 ppm ($-CH$ of the aromatic ring), 129.8 ppm (quaternary carbon of the aromatic ring attached to the substituted ethyl branch), 132.1 ppm (quaternary carbon of the central phenyl ring), 148.1 ppm (quaternary carbon of the aromatic ring linked to the sulfonate ester moiety).

B. Preparation of Organic–Inorganic Hybrid Materials. SBA-15 mesoporous silica was prepared according to the procedure described by Stucky and co-workers using poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) triblock copolymer (Pluronic 123) as the structure directing agent (SDA) and acid catalysis.[4] The SDA was removed quantitatively from the as-synthesized material by calcination at 500 °C overnight under air as was evidenced by TGA analysis and infrared spectroscopy.

Following calcination, the oxide was dried rigorously under a flow of helium at 200 °C during 15 h and transferred under argon in a Schlenk tube. The calcined SBA-15 silica material was characterized using classical methods such as XRD, nitrogen adsorption, and TGA analysis.

Grafting Reaction. The organosilane (~500 mg) was added to a suspension of SBA-15 (1 g) in dry toluene and stirred at 25 °C for 2 h and then heated at 90–100 °C. After several hours (2–4 h), volatiles including toluene and methanol (or ethanol) were distilled. The addition of fresh toluene, heating, and distillation sequences were repeated twice. The unreacted organic compound was then removed by a soxlhet extraction in CH_2Cl_2 overnight, and the resulting solid was finally dried in an oven at 70 °C overnight.

For **1·SBA**, [Si]$-$propyl$-$SH functional group: CP-MAS ^{13}C NMR, δ 8.7 ppm (Si$CH_2CH_2CH_2SH$), 27 ppm (Si$CH_2CH_2CH_2SH$), 48.9 ppm

($-OCH_3$); CP-MAS ^{29}Si NMR, δ -49 ppm (T[1]), -57 ppm (T[2]), -101.7 ppm (Q[3]), -110.5 ppm (Q[4]). Elemental analysis, wt % C, 2.4; S, 1.4.

For **2·SBA**, [Si]$-$propyl$-$SS$-$pyridyl functional group: CP-MAS ^{13}C NMR, δ 8.75 ppm (Si$CH_2CH_2CH_2SS-$), 22 ppm (Si$CH_2CH_2CH_2$-SS$-$), 41.5 ppm (Si$CH_2CH_2CH_2SS-$), 120.6, 138.1, 148.6, and 160.3 ppm (s, carbons of the pyridyl moiety); CP-MAS ^{29}Si NMR, δ -49 ppm (T[1]), -57 ppm (T[2]), -101.7 ppm (Q[3]), -110.5 ppm (Q[4]). Elemental analysis, wt % C, 7.3; S, 4.1; N, 0.57.

For **3·SBA**, [Si]$-$propyl$-$SS$-$propyl$-$[Si] functional group: CP-MAS ^{13}C NMR, δ 7.5 ppm (Si$CH_2CH_2CH_2SS-$), 21.8 ppm (SiCH_2CH_2-CH_2SS-), 41 ppm (Si$CH_2CH_2CH_2SS-$), 49.8 ppm ($-OCH_3$); CP-MAS ^{29}Si NMR, δ -41 ppm (T[0]), -49 ppm (T[1]), -57 ppm (T[2]), -95 ppm (Q[2]), -104 ppm (Q[3]), -113 ppm (Q[4]). Elemental analysis, wt % C, 6.0; S, 3.3.

For **4·SBA**, [Si]$-CH_2CH_2$aryl$-SO_3$Et functional group: CP-MAS ^{13}C NMR, δ 13.3 ppm (large singlet attributed to SiCH_2CH_2, SO_2-OCH_2CH_3, SiOCH_2CH_3), 28.3 ppm (SiCH_2CH_2), 58 ppm (SiOCH_2-CH_3), 67.2 ppm ($SO_2OCH_2CH_3$), 128 ppm ($-CH$ of the aromatic ring), 133 ppm (quaternary carbon of the aromatic ring attached to the ethyl chain), 151 ppm (quaternary carbon of the aromatic ring attached to the ethylsulfonate ester group); CP-MAS ^{29}Si NMR, δ -48 ppm (T[1]), -57 ppm (T[2]), -93 ppm (Q[2]), -102 ppm (Q[3]), -110 ppm (Q[4]). Elemental analysis, wt % C, 5.2; S, 1.2.

For **6·SBA**, [Si]$-CH_2CH_2$aryl$-SO_3-$aryl$-SO_3-$arylCH_2CH_2-[Si] functional group and related isomers: CP-MAS ^{13}C NMR, δ 16 ppm (large singlet, attributed to $-CH-$ and $-CH_2-$ carbons directly attached to a silicon atom and to $-CH_3$ carbons of not condensed ethoxysilane fragments), 24.1 ppm ($-CH$(Si)$-CH_3$), 28.4 ppm (Si$-$ CH_2-CH_2), 59 ppm (broad signal) (SiOCH_2CH_3), 123.9 ppm ($-CH$ of the central phenyl ring), 129.7 ppm ($-CH$ of the aromatic ring), 151 ppm (broad peak, quaternary carbons of the aromatic ring). Elemental analysis, wt % C, 2.7; S, 0.5.

Chemical Modification of the Grafted Species. Thiol Sites Generation by Cleavage of Disulfide Linkages. The reduction of disulfide bonds in **2·SBA** and **3·SBA** was achieved using a water-soluble trivalent phosphine, the tris(2-carboxyethyl)-phosphine (TCEP· HCl). Typically, 0.5–1 g of disulfide containing mesoporous silica materials was suspended in water, and a solution of TCEP (2 equiv of TCEP per disulfide unit) in water and methanol (1:2) was added via a syringe at room temperature. The mixture was stirred at 25 °C for 1 h, warmed at 55 °C, and kept at that temperature for 1–3 days. After filtration, the solid was sequentially washed with water and methanol to remove the unreacted phosphine and the organic reaction products.

For **7·SBA**, [Si]$-$propyl$-$SH functional group: CP-MAS ^{13}C NMR, δ 10 ppm (Si$CH_2CH_2CH_2SH$), 27.5 ppm (Si$CH_2CH_2CH_2SH$), 50.7 ppm ($-OCH_3$). CP-MAS ^{29}Si NMR, δ -57 ppm (T[2]), -66 ppm (T[3]), -93 ppm (Q[2]), -100.1 ppm (Q[3]), -110.5 ppm (Q[4]). Elemental analysis, wt % C, 2.7; S, 2.0.

For **8·SBA**, [Si]$-$propyl$-$SH HS$-$propyl$-$[Si] functional groups: CP-MAS ^{13}C NMR, δ 10 ppm (Si$CH_2CH_2CH_2SH$), 27.5 ppm (Si$-$ $CH_2-CH_2-CH_2-SH$), 51 ppm ($-OCH_3$). CP-MAS ^{29}Si NMR, δ -47 ppm (T[1]), -57 ppm (T[2]), -66 ppm (T[3]), -91.6 ppm (Q[2]), -101 ppm (Q[3]), -119.7 ppm (Q[4]). Elemental analysis, wt % C, 3.4; S, 2.7.

Sulfonic Acid Active Site Generation. (a) Oxidation of the Corresponding Thiol. The oxidation of mercaptopropyl groups of **7·** **SBA** and **8·SBA** was performed using the procedure described by Stucky and co-workers.[4] First, 0.3 g of the thiol containing material was suspended in 10 g of aqueous 30 wt % H_2O_2, and the suspension was stirred at 25 °C overnight under an argon atmosphere. The subsequent acidification was carried out in 1 M H_2SO_4 solution at the same temperature for 2 h. Finally, the solid was washed with water and ethanol and dried at 70 °C.

For **9·SBA**, [Si]$-$propyl$-SO_3H$ functional group: CP-MAS ^{13}C NMR, δ 10 ppm (Si$CH_2CH_2CH_2SO_3H$), 17.9 ppm (Si$CH_2CH_2CH_2$-SO_3H), 54 ppm (Si$CH_2CH_2CH_2SO_3H$). In addition to these resonances, peaks with weak intensity were also observed at 23, 37.5, and 64 ppm

attributed to disulfide and partially oxidized species. CP-MAS ^{29}Si NMR, δ −57.5 ppm (T^2), −66.8 ppm (T^3), −92 ppm (Q^2), −101 ppm (Q^3), −110.5 ppm (Q^4). Elemental analysis, wt % C, 1.9; S, 1.4.

For **10·SBA**, [Si]−propyl−SO$_3$H HO$_3$S−propyl−[Si] functional group: CP-MAS ^{13}C NMR, δ 10 ppm (SiCH$_2$CH$_2$CH$_2$SO$_3$H), 17.9 ppm (SiCH$_2$CH$_2$CH$_2$SO$_3$H), 54 ppm (SiCH$_2$CH$_2$CH$_2$SO$_3$H). In addition to these resonances, peaks with weak intensity were also observed at 23, 37.5, and 64 ppm attributed to disulfide and partially oxidized species. CP-MAS ^{29}Si NMR, δ −58 ppm (T^2), −66 ppm (T^3), −92 ppm (Q^2), −101 ppm (Q^3), −110.5 ppm. Elemental analysis, wt % C, 2.5; S, 1.7

(b) Sulfonate Ester Transformation. The hydrolysis of the sulfonate ester moiety in **4·SBA** and **6·SBA** was carried out with a H$_2$SO$_4$ aqueous solution (1 wt %) at 60 °C during 15 h. The solid was then filtered, washed carefully with a large amount of water, and dried at 80 °C in an oven.

For **11·SBA**, [Si]−CH$_2$CH$_2$aryl−SO$_3$H functional group: CP-MAS ^{13}C NMR, δ 12 ppm (large singlet attributed to SiCH$_2$CH$_2$), 28 ppm (s, SiCH$_2$CH$_2$), 127 and 128 ppm (−CH of the aromatic ring), 140 ppm (quaternary carbon of the aromatic ring attached to the ethyl chain), 148 ppm (quaternary carbon of the aromatic ring attached to the sulfonic acid group). CP-MAS ^{29}Si NMR, δ −57 ppm (T^2), −67.4 ppm (T^3), −91 ppm (Q^2), −100.7 ppm (Q^3), −111 ppm (Q^4). Elemental analysis, wt % C, 2.5; S, 0.8.

For **12·SBA**, [Si]−CH$_2$CH$_2$aryl−SO$_3$H HO$_3$S−arylCH$_2$CH$_2$−[Si] functional group: CP-MAS ^{13}C NMR, δ 12.8 ppm (large singlet attributed to SiCH$_2$CH$_2$), 28 ppm (SiCH$_2$CH$_2$), 128 ppm (−CH of the aromatic ring), 140 ppm (quaternary carbon of the aromatic ring attached to the ethyl chain), 148 ppm (quaternary carbon of the aromatic ring attached to the sulfonic acid group). Elemental analysis, wt % C, 2.2; S, <0.5.

Characterization. X-ray powder diffraction (XRD) data were acquired on a BRUCKER D5005 diffractometer using Cu K$_\alpha$ radiation (λ = 1 054 184 Å). A Netzsch thermoanalyzer STA 449C was used for simultaneous thermal analysis combining thermogravimetric (TGA) and differential thermoanalysis (DTA) at a heating rate of 10 °C/min in air. Nitrogen adsorption and desorption isotherms were measured at 77 K. All of the organic−inorganic hybrids were evacuated at 180 °C for 24 h before the measurements. Specific surface areas were calculated following the BET procedure. Pore size distribution was obtained by using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherm. Elemental analyses for C, S, and N were performed by Quantitative Technologies Inc., NJ.

Solid-state CP MAS ^{13}C and ^{29}Si NMR measurements were recorded on a Bruker Avance DSX-200 spectrometer operating at 200.2, 50.3, and 39.8 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively, and using a Bruker 7 mm CP MAS probe. A typical spinning rate for CP MAS experiments is 4 kHz. A 2 ms cross polarization contact time was used to acquire ^{29}Si and ^{13}C CP MAS spectra with a repetition delay of 1.5 and 32 000 scans. ^{13}C and ^{29}Si MAS spectra were referenced to tetramethylsilane.

Liquid NMR spectra were recorded on a Varian Mercury-300 spectrometer. All chemical shifts were measured relative to residual ^{1}H or ^{13}C NMR resonances in the deuterated solvents: C$_6$D$_6$, δ 7.15 ppm for ^{1}H, 128 ppm for ^{13}C; CD$_2$Cl$_2$, δ 5.32 ppm for ^{1}H, 53.8 ppm for ^{13}C.

The acid capacities of the sulfonic acid mesoporous materials were determined by ion-exchange with an aqueous solution of sodium chloride (NaCl, 2 M; suspension allowed to equilibrate during 24 h) followed by titration with a solution of 0.01 N NaOH (aq).

Catalytic Experiments. The condensation of phenol and acetone to produce bisphenol A was carried out in a sealed glass vessel at 85 °C during 24 h. The solid catalysts were dried at 90 °C under vacuum overnight prior to the catalytic experiments. A typical experiment consisted of 5−7 g of phenol and 0.5−1 g of acetone with 0.07−0.1 g of sulfonic acid containing SBA-15 silica materials.

At the end of the reaction, the products were analyzed by both gas chromatography and liquid NMR spectroscopy. In the case of GC analysis, biphenyl in acetonitrile was used as an external standard. The suspension was first centrifuged, and the resulting solution was analyzed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector and a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). For the NMR analysis, mesitylene in CD$_3$OD was used as an external integration standard. The quantification of the products in this case was based on the methyl peaks of the products and mesitylene.

Supporting Information Available: ^{1}H NMR spectra of the molecular precursors **5** and **6**: hydrosilylation of **5**. ^{13}C CP-MAS NMR spectra of **4·SBA** and **11·SBA**: transformation of the sulfonate ester to the sulfonic acid. ^{29}Si CP-MAS NMR spectra of **4·SBA** and **11·SBA**: transformation of the sulfonate ester to the sulfonic acid. ^{29}Si CP-MAS NMR spectra of **2·SBA** and **7·SBA**: cleavage of the disulfide linkage of the disulfide functionalized **2·SBA**. ^{29}Si CP-MAS NMR spectra of **3·SBA** and **8·SBA**: cleavage of the disulfide linkage of the disulfide functionalized **3·SBA**. Powder X-ray diffraction patterns of (a) transformation of ethylsulfonate **4·SBA** into sulfonic acid **11·SBA**; (b) cleavage of disulfide bond in **2·SBA** to produce surface thiol species **7·SBA**; (c) cleavage of disulfide bond in **3·SBA** to produce surface thiol species **8·SBA**. TGA measurements of **1·SBA**, **2·SBA**, **3·SBA**, and **4·SBA** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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