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Enhanced cooperative, catalytic behavior of organic functional groups by immobilization

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Abstract

The addition of thiol to the sulfonic acid-catalyzed condensation of phenol and acetone to give bisphenol A is investigated using homogeneous and SBA-15-immobilized sulfonic acids. Inclusion of thiols into the reaction media of either type of sulfonic acid catalyst accelerates the rate of reaction and shifts the regioselectivity to favor the formation of the p,p'-bisphenol isomer (bisphenol A) over the unwanted o,p'-bisphenol isomer. By immobilizing the thiol on the same solid as the sulfonic acid, reaction rates and regioselectivities are enhanced even further from those obtained from using mixtures of these two functional groups (when they are both homogeneous, or a combination of homogeneous and heterogeneous). A mechanism is proposed to explain the reactivity and involves cooperative interactions via the proximity of the immobilized sulfonic acid and the immobilized thiol. This enhanced reactivity can only be achieved by immobilizing the two functional groups on a solid.

Keywords: Bifunctional catalyst; Heterogeneous; Bisphenol A; Functionalized SBA-15

1. Introduction

A current area of interest in the design and synthesis of solid catalysts is the creation of materials that contain multiple types of active centers. These functionalities may be used to perform several steps in a reaction sequence or work in a cooperative manner to alter the characteristics (e.g., rates, selectivities) of a single reaction. Dufaud and Davis recently showed that alkyl sulfonic acid modified SBA-15 derived from the cleavage and oxidation of a dipropyl disulfide modified SBA-15 was more active (approximately two-fold) and regioselective for the synthesis of p,p'-bisphenol from phenol and acetone than its monosite or homogeneous analogue [1]. They claimed that this enhanced catalytic behavior was from some type of cooperativity between sites, but were unable to conclusively determine the origin of these effects. Solid-state nuclear magnetic resonance (NMR) data revealed only the presence of the sulfonic acid functional groups. However, the number of acid sites measured by titration was lower than the number of sulfur groups obtained by elemental analysis. Because it is difficult to achieve quantitative conversion of thiols to sulfonic acids by oxidation with hydrogen peroxide (the method used by Dufaud and Davis), cooperative effects between thiol and sulfonic acid functional groups cannot be ruled out as the origin of the enhanced catalytic behavior (rather than two sulfonic acid groups). If this is the case, then the catalytic entities must have significantly enhanced reactivity to give such a large overall increase in rate because the number of these cooperative interactions must have been very small.

There is a long history of combining thiol-containing molecules to sulfonic acid containing polymeric resins to produce catalysts for the condensation of phenol and acetone to produce bisphenol A [2–5]. More recently, the thiol and sulfonic acid centers have been placed on either polymeric resins [6] or polysiloxanes [7]. The role of thiol for this reaction remains unclear from the literature with both positive and negative effects being reported [8].

Here, we explore whether or not the origin of the enhanced catalytic behavior observed by Dufaud and Davis is due to immobilized thiol groups in close proximity to sulfonic acid

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groups. Our results strongly suggest that the immobilization of a thiol in proximity to a sulfonic acid creates an extremely effective catalytic entity that exploits cooperative behavior between the two types of functional groups to achieve reaction rates and regioselectivities that cannot be obtained without immobilization. These types of reactive centers are most likely the origin of the enhanced reactivity observed by Dufaud and Davis.

2. Experimental

All reactions were run under an inert argon atmosphere. Silane reagents were purchased from Gelest and used as obtained. P123 was purchased from Aldrich (MW 5800). Sulfonic acids were purchased from Aldrich as sodium salts and acidified with concentrated HCl before use. High-pressure liquid chromatography (HPLC) analysis was done on a HP 1100 series instrument with a C18 Prevail reverse-phase column and measuring UV–vis absorption at 272 nm. A representative HPLC trace is available in the supporting information.

2.1. "One-pot" oxidation synthesis

P123 (1.99 g, 0.344 mmol), followed by 2.0 M HCl (60.0 mL, 120 mmol) and water (3.0 mL, 166.5 mmol), were added to a Teflon bottle. This mixture was stirred at 40 °C until the P123 was fully dissolved. Tetraethoxysilane (4.1 mL, 18.9 mmol) was then added, and the resulting cloudy white solution was stirred for 45 min at 40 °C. Hydrogen peroxide (2.1 mL, 30 wt% solution) was then added, followed by mercaptopropyltrimethoxysilane (0.38 mL, 2.0 mmol). The solution was stirred at 40 °C for 20 h and then aged under static conditions at 100 °C for 24 h. The solid white product was isolated by filtering under an aspirator and rinsing with copious amounts of water (3 × 300 mL). The product was dried under an aspirator overnight. The as-synthesized material was then refluxed in EtOH (400 mL EtOH/g solid catalyst) for 24 h to remove P123. The extracted product was then filtered, rinsed with copious amounts of EtOH (3 × 300 mL), and dried under an aspirator overnight. The solid was then further dried under vacuum at 80 °C and stored under Ar.

2.2. One-pot synthesis

Outlined below is a general procedure for the one-pot method of producing the organically functionalized SBA-15-DF catalysts. P123 (4.0 g, 0.688 mmol) was weighed into a Teflon bottle. Then 2.0 M HCl (120.0 mL, 240.0 mmol) and H_2O (6.0 mL, 333.0 mmol) were added, and the mixture was stirred at 40 °C until the P123 was fully dissolved. TEOS (8.2 ml, 37.8 mmol) was then added to the reaction and stirred at 40 °C for 45 min prehydrolysis time. The two silanes were then added in the desired amounts and relative ratios. For catalyst 1, 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane (0.65 g, 50/50 w/w solution in dichloromethane, 1.0 mmol) was added first to allow for hydrolysis of the sulfonyl chloride, followed by 3-mercaptotrimethoxysilane (0.19 mL, 1.0 mmol). The remaining catalysts were prepared in the same manner, changing the relative ratio of these two precursors. The mixture was stirred at 40 °C for 20 h, aged at 100 °C for 24 h, and then cooled to room temperature. The resulting solid was filtered and repeatedly rinsed with excess H_2O (4 × 500 mL). The solid was then allowed to dry overnight on an aspirating filter. The dried solid was extracted with EtOH (400 mL/g) by refluxing in EtOH for 24 h to remove P123. The solid was once again filtered and rinsed repeatedly with EtOH (4 × 500 mL), then dried overnight on the aspirator to obtain a dry white solid. Finally, the solid was further dried at 80 °C under vacuum for 24 h and stored under Ar.

2.3. Characterization

Solid-state NMR spectra were recorded using a Bruker Advance 200-MHz spectrometer with spinning at 4 KHz (Bruker 7-mm CP MAS probe). A 2-ms cross-polarization contact time was used to acquire ^{29}Si and ^{13}C spectra with a repetition delay of 1.5 s and 32,000 scans. Powder X-ray diffraction (XRD) data were acquired on a Brucker D5005 diffractometer using Cu-K_α radiation. Nitrogen adsorption and desorption isotherms were measured at 77 K. Samples were dried at 100 °C for 12 h before analysis. Surface areas were calculated using the BET procedure. Pore size distribution was calculated using the BJH pore analysis applied to the desorption branch of the isotherm. XRD and N_2 adsorption were carried out at the Institute of Research on Catalysis, Lyon, France. Elemental analysis was carried out by QTI Technologies, Whitehouse, NJ.

The acid capacities of the sulfonic acid functionalized mesoporous materials were determined by ion exchange with an aqueous solution of sodium chloride (2 M) for 24 h. The resulting suspension was then filtered, rinsed with water, and the filtrate was titrated with 0.01 N NaOH (aq) with phenol red as an indicator.

Thiol content was determined by the Ellman's titration assay [11]. Sodium phosphate dibasic buffer was prepared in water (0.1 M). The thiol containing mesoporous material (1–3 mg) was suspended in sodium phosphate buffer (4.0 mL) and then a solution of Ellman's reagent in sodium phosphate buffer (1.0 mL, 4 mg/mL) was added to this solution. The resulting solution was incubated at room temperature over 4 h to allow for complete exchange. After 4 h, the solution was diluted (1:3 dilution) with sodium phosphate buffer and the absorption at 412 nm was recorded. The concentration of thiol was then determined using an experimentally determined extinction coefficient of 13,600 $M^{-1}\,cm^{-1}$.

2.4. Catalytic experiments

Catalytic reactions were carried out in sealed vials under an Ar atmosphere. Catalyst was tared into an oven-dried vial (typically 100–300 mg, 0.01 eq) and the catalyst was then dried under vacuum at 80 °C for 12 h before use. Phenol (typically ∼1.6 g, 3.5 eq) was then added to the reaction, followed by acetone (typically ∼350 μL, 1.0 eq). The reaction was then

sealed under Ar and heated at 100 °C for 24 h. The reaction was then quenched by addition of a carefully measured amount of acetonitrile (∼10 mL). This diluted reaction was then further diluted for HPLC analysis (typically 100 μL reaction +700 μL acetonitrile); see Supporting Information for representative chromatogram. This was done with an isocratic method of 60:40 H_2O:ACN (0.01% TFA). Phenol elutes at 5.9 min, BPA at 13.1 min, and o,p isomer at 22.0 min using this method. Conversion was then quantified using a diode array detector based on a standardized calibration curve for BPA.

3. Results and discussion

The nature of the cooperative effect observed by Dufaud and Davis for the condensation reaction between phenol and acetone to give bisphenol A was not conclusively defined. Two possibilities were presented: (i) cooperative effects between two sulfonic acid functional groups in close proximity, or (ii) the cooperativity between small amounts of thiol sites remaining on the solid from incomplete oxidation and the formed sulfonic acids [1]. In an attempt to distinguish between these two possibilities, the effects of thiols on homogeneous and heterogeneous sulfonic acid catalyst systems are investigated here.

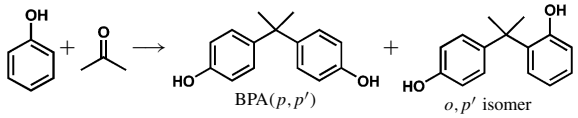
The effects of added thiol on the homogeneous condensation of phenol and acetone to bisphenol A were investigated using a variety of homogeneous sulfonic acid-based catalysts (Table 1). The reaction catalyzed by 1-propane sulfonic acid (excess phenol, 0.01 eq of acid per acetone, entry 1) results in 18% conversion of acetone to bisphenol A. Nearly equivalent quantities of the two isomers are observed ($p,p'/o,p' = 1.4$). When a mixed 1:1 acid/thiol catalyst system was employed (Table 1, entry 2), a very marked increase in the per site yield (from 18.2 to 50.6) and selectivity for the desired p,p'-isomer is observed ($p,p'/o,p' = 6.6$). Table 1, entry 3 illustrates that even with a 2:1 ratio of sulfonic acid to thiol, significant enhancements to selectivity and reactivity are observed. Note that the thiol alone does not promote the condensation; Table 1, entry 11. For this reaction, the selectivities can be compared at different levels of conversion because the selectivity is independent of conversion (see supporting information).

Molecules containing thiol and acid functional groups separated by an alkyl chain were investigated also (Table 1, entries 4 and 5). Whereas the length of the intramolecular tether (entry 4 vs. entry 5) appears to only have a minor effect on reactivity, the fact that the two functional groups are located within the same molecule does result in a major increase in reactivity and regioselectivity to bisphenol A. Per site yields (PSY) >60 are achieved with higher selectivity for the p,p'-isomer (>7) when the thiol and sulfonic acid are contained within the same molecule.

No significant differences are observed between a single sulfonic acid site and two sulfonic acid sites when they are present within the same molecule (Table 1, entry 6). Comparing entry 6 and entry 1 of Table 1, it is shown that for the tethered acid sites the PSY changes very little (from 18.2 to 20.0) compared to untethered sites; although small effects on selectivity are obtained $p,p'/o,p'$ ratio vary from 1.4 to 2.3). Employment of the diacid catalyst in the presence of propane thiol causes the conversion and selectivity to again show dramatic improvements over the diacid alone (Table 1, entry 8). The data in Table 1 clearly demonstrate the enhanced reactivity and regioselectivity obtained from homogeneous sulfonic acid catalysts by the presence of thiols.

Guided by the homogeneous data, the effects of added thiol on heterogeneous reactions were investigated and the results are listed in Table 2. A SBA-15 supported analogue of 1-propane sulfonic acid was prepared by a one-pot synthetic method using mercaptopropyltrimethoxysilane as the source of the thiol and oxidizing it in situ with hydrogen peroxide as reported in the literature [9]. The supported acid catalyst is less active than the homogeneous catalyst on a per acid site basis (PSY = 4.9 vs. 18.2) and shows no significant advantage in terms of selectivity for the desired p,p'-isomer (Table 2, entry 1 vs. Table 1, entry 1). The addition of mercaptopropane to the reaction mix-

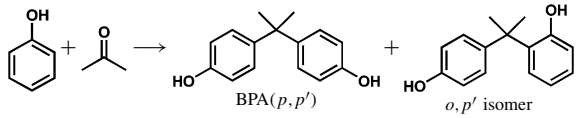
Table 1
Effect of thiol on homogeneous catalysis with sulfonic acids (PSY = per site yield)



Entry	Catalyst (eq)	Additive (eq)	Conversion BPA (%)	Conversion o,p' (%)	p,p':o,p'	PSY
1	SO_3H (0.01)	–	10.7	7.5	1.4:1	18.2
2	SO_3H (0.01)	SH (0.01)	44.0	6.6	6.6:1	50.6
3	SO_3H (0.01)	SH (0.005)	40.9	8.4	4.9:1	49.3
4	HO_3S SH (0.01)	–	54.7	6.9	7.9:1	61.6
5	HO_3S SH (0.01)	–	57.8	7.7	7.5:1	65.5
6	HO_3S SO_3H (0.01)	–	33.6	7.7	4.4:1	20.0
7	HO_3S SO_3H (0.005)	–	14.1	6.0	2.3:1	20.1
8	HO_3S SO_3H (0.01)	SH (0.005)	53.9	9.4	5.7:1	31.7
9	HO_3S SO_3H (0.005)	SH (0.005)	40.5	6.6	6.1:1	47.1
10	HO_3S SO_3H (0.005)	–	15.7	6.8	2.3:1	22.5
11	–	SH (0.01)	0.0	0.0	–	0.0

Reaction conditions: 3.5 eq phenol, 1.0 eq acetone, 0.01 eq sulfonic acid, 100 °C, 24 h. Yields determined by HPLC quantification of BPA and o,p' isomer production. Conversion calculated based on acetone as limiting reagent. Per site yield calculated per sulfonic acid site.

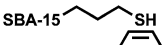
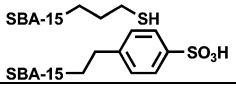
Table 2
Effect of thiol on heterogeneous, sulfonic acid catalysis



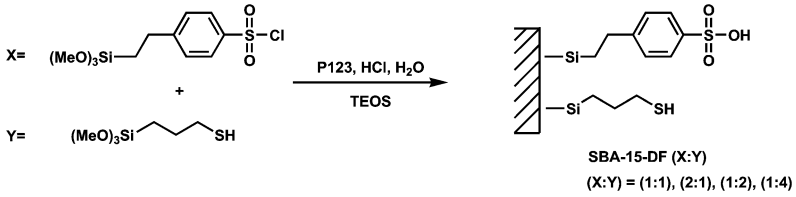
Entry	Catalyst (eq)	Additive (eq)	Conversion BPA (%)	Conversion o,p' (%)	p,p':o,p'	Per site yield
1	SBA-15–SO_3H (0.01)	–	3.3	1.6	2.1:1	4.9
2	SBA-15–SO_3H (0.01)	SH (0.01)	13.2	1.8	7.5:1	15.0
3	SBA-15–SO_3H (0.01)	SH (0.0025)	12.2	1.9	6.2:1	14.1

Reaction conditions: 3.5 eq phenol, 1.0 eq acetone, 0.01 eq sulfonic acid, 100 °C, 24 h. Yields determined by HPLC quantification of BPA and o,p' isomer production. Conversion calculated based on acetone as limiting reagent. Per site yield calculated per sulfonic acid site.

Table 3
Structural and textural characterization of solid SBA-15 catalysts

Entry	Sample	XRD		N_2 adsorption	
		d_{100}[a] (A)	Wall thickness[b] (Å)	D_p[c] (Å)	S_{BET} (m^2/g)
1	SBA-15-DF (1:1)	96.4	49.1	62.2	827
2	SBA-15-DF (2:1)	110.7	65.1	62.7	753
3	SBA-15-DF (1:2)	95.3	56.8	53.2	783
4	SBA-15-DF (1:4)	84.9	50.6	47.4	666
5		98.1	59.2	54.1	838
6		103.1	43.9	75.1	782

[a] $d(100)$ spacing.
[b] Calculated by (a_0− pore size), where $a_0 = 2d_{100}/\sqrt{3}$.
[c] Pore size determined from desorption branch using the BJH method of analysis.



Scheme 1. Synthesis of thiol/sulfonic acid functionalized SBA-15.

ture gives a significant enhancement in catalyst performance, both in terms of PSY and selectivity (Table 2, entry 2). Relatively small quantities of added thiol produce similar effects with the solid and homogeneous catalysts. Table 2, entry 3 shows data from a 4:1 ratio of sulfonic acid:thiol and the effect of the thiol is still dramatic. As with the homogeneous catalysts, selectivity is also independent of conversion for the solid catalysts (see supporting information). It is clear from these data that the thiol is responsible for dramatic increases in selectivity for bisphenol A as well as enhances in the rate of its formation with the solid catalyst.

The catalytic data listed in Tables 1 and 2 suggest that a solid catalyst with thiol and sulfonic acid sites neighboring each other could potentially give enhanced conversions and selectivities over the sulfonic acid site alone. To examine this hypothesis, one-pot syntheses of SBA-15 that simultaneously incorporate sulfonic acid and thiol functional groups through co-crystallization were used to create a set of solid materials that immobilize these two functional groups at varying ratios. By adding 3-mercaptopropyltrimethoxysilane and 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane (sulfonyl chloride hydrolyzes under acidic synthesis conditions) to a mixture of TEOS, 2.0 M HCl, H_2O, and P123 (53:348:484:1), SBA-15 functionalized with thiol and sulfonic acid was obtained (Scheme 1). This procedure was repeated with varying ratios of thiol to sulfonic acid precursor in the one-pot synthesis to give dual-functionalized SBA-15 catalysts [denoted as SBA-15-DF (X:Y), where X represents the relative amount of acid and Y the relative amount of thiol].

The obtained solids were characterized by XRD (see supporting information) and N_2 adsorption analysis (see supporting information for a representative adsorption/desorption isotherm) after extraction of the P123 (Table 3). The XRD patterns show that in all cases the one-pot synthesis produces highly ordered materials with the same hexagonal morphology as SBA-15 (see supporting information). The N_2 adsorption data illustrate the large pore size of these solids (54–70 Å) and BET surface areas on the order of 800 m^2/g, very similar to those for unmodified SBA-15 [9].

Solid-state ^{13}C CP/MAS NMR was used to confirm the presence of the organic functional groups. Fig. 1 shows NMR spectra that clearly reveal the presence of the propyl thiol and aro-

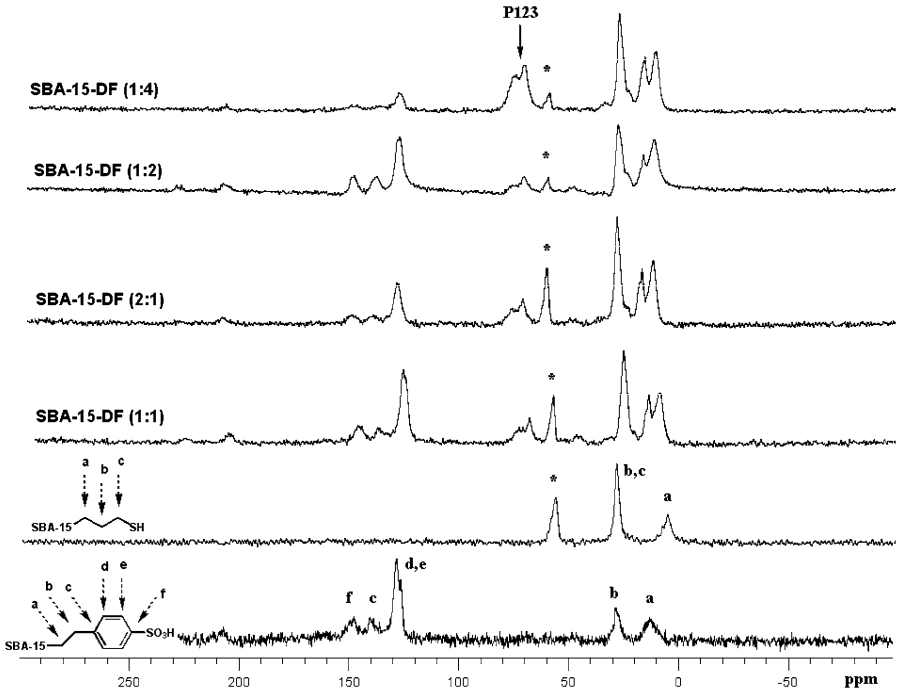


Fig. 1. ^{13}C solid state NMR of the dual functionalized SBA-15 solids after EtOH extraction. Residual methoxy (Si(OMe)) denoted with *.

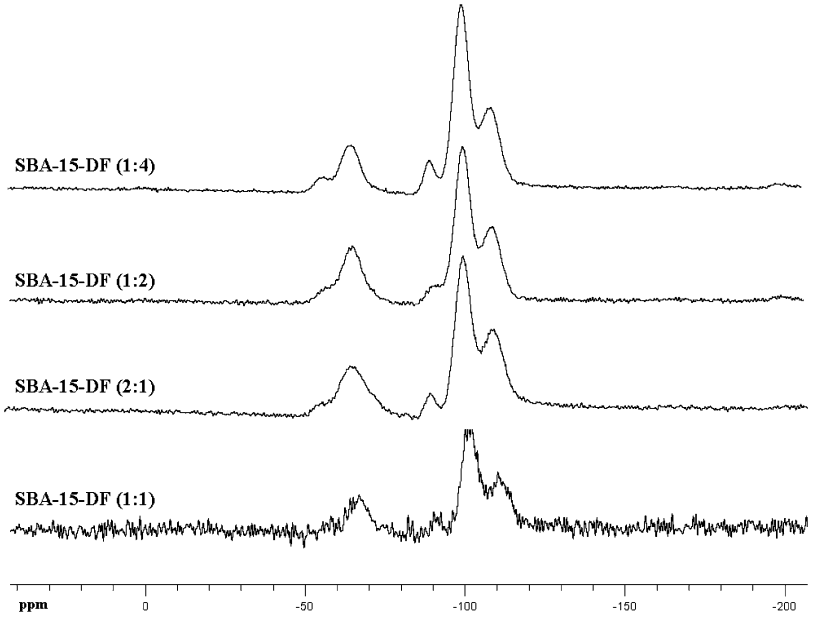


Fig. 2. ^{29}Si NMR of dual functionalized SBA-15 solids.

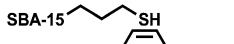
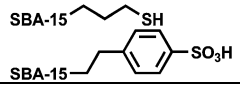
matic sulfonic acid groups. Even though it is difficult to make quantitative comparisons from CP NMR data, the relative intensity of the peaks also correspond roughly to the relative ratio of functional groups used in the synthesis. The resonances at 72–78 ppm are due to trace amounts of the P123 surfactant remaining after the extraction process, whereas the small peaks far downfield around 220 ppm are spinning sidebands.

Solid-state ^{29}Si CP/MAS NMR was performed on all SBA-15-DF catalysts to confirm the presence of silicon–carbon bonds. Fig. 2 shows the ^{29}Si CP/MAS NMR spectra of all four SBA-15-DF catalysts; the data reveal quaternary silicon atoms of the SBA-15 support (Q^3 and Q^4 at −100 and −110 ppm, respectively) in addition to the tertiary silicon atoms (T^1 and T^2 at −55 and −65 ppm, respectively). This degree of condensation and the absence of T^0 sites demonstrate that all of the organic groups are covalently bound to the SBA-15 support.

Sulfonic acid-bearing catalysts were titrated with NaOH after ion exchange with 2 M aqueous NaCl using phenol red as an indicator [1,10], whereas the thiol content was determined using Ellman's reagent titration protocol [11]. These data, as well as elemental analyses data, are presented in Table 4.

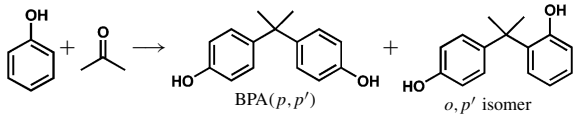
Entries 1–4 in Table 4 demonstrate that the two functional groups are incorporated into the SBA-15-DF catalysts and are accessible and reactive (due to the nature of the titrations). En-

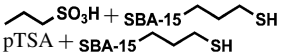
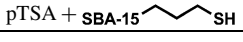
Table 4
Quantitative analysis of the solid materials containing both thiol and sulfonic acid functional groups

Entry	Catalyst	Theoretical SO_3H:SH	SO_3H titration[a] (mmol/g)	SH titration[b] (mmol/g)	Observed ratio	S from titrations (%)	S from E.A.[c] (%)
1	SBA-15-DF (1:1)	1:1	0.33	0.34	1:1	2.2	2.5
2	SBA-15-DF (2:1)	2:1	0.47	0.35	1.4:1	2.6	3.3
3	SBA-15-DF (1:2)	1:2	0.32	0.64	1:2	3.1	4.1
4	SBA-15-DF (1:4)	1:4	0.16	0.83	1:5.3	3.2	3.3
5		–	–	0.90	–	2.9	3.2
6		–	0.59	–	–	1.6	1.6

[a] Acid titration done by exchanging with NaCl and then titrating resulting solution with NaOH.
[b] SH titration done with Ellman's reagent and measured absorbance at 412 nm.
[c] Elemental Analysis done by QTI of N.J. Values reported are ±0.3%.

Table 5
Reactivity results from solid catalysts



Entry	Catalyst (eq)	Ratio (acid:SH)	BPA (%)	o,p' (%)	p,p':o,p'	PSY
1	SBA-15-DF (1:1)	1:1	70.6	4.0	17.3:1	74.6
2	SBA-15-DF (2:1)	2:1	60.0	5.0	12.0:1	65.0
3	SBA-15-DF (1:2)	1:2	78.0	3.9	19.8:1	81.9
4	SBA-15-DF (1:4)	1:4	71.3	4.4	16.3:1	75.7
5	Phys. Mix.	1:1	14.6	4.9	3.0:1	19.5
6	pTSA	–	20.5	5.1	4.0:1	25.6
7		1:1	25.6	5.7	4.5:1	31.3
8		1:1	29.5	7.2	4.1:1	36.7

Reaction conditions: 3.5 eq phenol, 1.0 eq acetone, 0.01 eq sulfonic acid, 100 °C, 24 h. Yields determined by HPLC quantification of BPA and o,p' isomer production. Conversion calculated based on acetone as limiting reagent. Per site yield calculated per sulfonic acid site. pTSA = *para*-toluenesulfonic acid. Entry 5 is a physical mixture of SBA-propyl-SH and SBA-SO_3H in a 1:1 ratio.

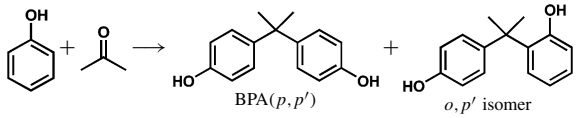
tries 5 and 6 of Table 4 are from the monofunctionalized materials. When reporting PSY with these materials, the titration data were used to determine catalyst loadings.

The solid catalysts were used to test the hypothesis that immobilized thiol and sulfonic acid functional groups may reveal enhanced reactivity for the condensation reaction between phenol and acetone. Catalytic data from the solids listed in Table 4 are given in Table 5. SBA-15-DF (1:1) gives an increase in selectivity of 17.3:1 for bisphenol A (Table 5, entry 1), a rate far superior to that achieved with the homogeneous catalysts and close to that of the best cases in the homogeneous reaction (Table 1, entries 3 and 4). As with homogeneous catalysis, the selectivities are independent of the level of conversion for the solid catalysts (see supporting information) and thus allow for comparisons at varying conversions. For the case where the surface is functionalized with excess sulfonic acid (Table 5, entry 2), reactivity and selectivity are still significantly better than those from immobilized sulfonic acid alone (Table 2, entry 1). Using excess thiol relative to sulfonic acid (Table 5, entry 3) further increases the selectivity to nearly 20:1 and gives the highest rate of conversion of all of the catalysts prepared in this study (PSY = 81.9). Further increases in the ratio of thiol to acid (Table 5, entry 4) decrease the selectivity and reactivity. Table 5, entry 5 shows data from a physical mixture of the two monofunctional groups isolated on separate SBA-15 solids and used in a 1:1 ratio in the condensation reaction. For this case, the reactivity and selectivity are reduced to the levels of the acid alone. This result strongly supports a cooperative effect occurring on the surface between sulfonic acid and thiol sites in close proximity, as segregating the functional groups diminishes any enhancements to reactivity. Entry 6 (Table 5) was carried out using only *para*-toluenesulfonic acid (pTSA) in solution for comparison. Entries 7 and 8 (Table 5) were from immobilized thiol functional groups on SBA-15 with propane sulfonic acid and pTSA, respectively, added homogeneously. In these cases, the reactivity and selectivity improve slightly, but not nearly as much as with entries 1–4 of Table 5. Based on these data, we conclude that there must be a cooperative effect between the functional groups that is enhanced by their immobilization in proximity to one another.

The reactivity data from the SBA-15 immobilized thiol and sulfonic acid functionalities suggest that the rate and selectivity enhancements observed by Dufaud and Davis could in fact have been due to a small amount of these functional groups in close proximity to each other. While the number of these sites may have been small, their superior reactivity could most certainly have provided the observed enhancements.

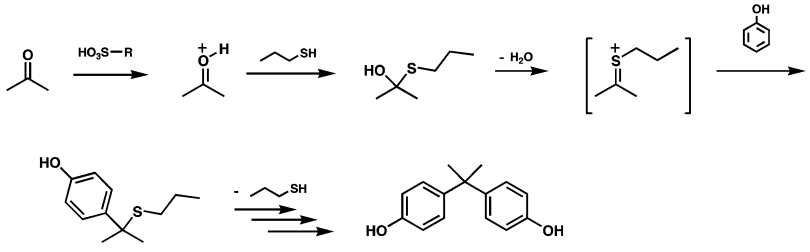
In an attempt to rationalize the role of thiol in the formation of bisphenol A, a plausible mechanism to explain the increases in reaction rate as well as selectivity is shown in Scheme 2.

Table 6
Steric effects of thiol



Entry	Catalyst (eq)	Additive (eq)	Conversion BPA (%)	Conversion o,p (%)	p,p':o,p'	PSY
1	SO_3H (0.01)	SH (0.01)	8.8	5.7	1.5:1	14.5
2	SO_3H (0.01)	SH (0.01)	45.3	6.4	7.1:1	51.7
3	SBA-15 SO_3H (0.01)	SH (0.01)	2.9	1.0	2.8:1	3.9
4	SBA-15 SO_3H (0.01)	SH (0.01)	12.7	1.1	11.1:1	13.8

Reaction conditions: 3.5 eq phenol, 1.0 eq acetone, 0.01 eq sulfonic acid, 100 °C, 24 h. Yields determined by HPLC quantification of BPA and o,p isomer production. Conversion calculated based on acetone as limiting reagent. Per site yield calculated per sulfonic acid site.



Scheme 2. Possible mechanism for thiol involvement in the condensation reaction of phenol and acetone.

Given the nucleophilicity of sulfur, it is possible that thiol further activates the carbonyl of acetone to nucleophilic attack by phenol via a charged sulfur intermediate. This not only could increase the electrophilicity of the carbonyl causing increases in reaction rate, but also could put the side chain of the thiol in a position adjacent to the site of electrophilicity to affect the approach of phenol and give rise to increased selectivity.

The effect of the steric nature of the thiol was examined; results are given in Table 6. If the proposed mechanism is correct, then the steric nature of the thiol could have dramatic effects on selectivity and reactivity. A bulky thiol, such as t-butylthiol, no longer enhances the selectivity and conversion (Table 6, entry 1). However, a more sterically accessible thiol, such as benzyl mercaptan, causes significant improvements in rate and selectivity (Table 6, entry 2). Entries 3 and 4 in Table 6 further illustrate the dramatic effect of sterics on selectivity and reactivity in this reaction when different thiols are added with immobilized sulfonic acid sites. Although these results do not provide direct proof of the proposed mechanism, they do indicate the importance of the steric nature of the thiol and support the proposed mechanism. If the two functional groups are tethered to the surface near each other, then on activation of acetone by protonation, the thiol would not have to diffuse to the reaction center, because it would be immobilized very close to the acid site. Further mechanistic insight is the objective of current work, which will be reported in due course.

4. Conclusion

An examination of the role of thiol in the sulfonic acid-catalyzed condensation of acetone and phenol to form bisphenol A has been conducted. Based on findings from homogeneous reactions, bifunctional solid materials bearing thiol and sulfonic acid functional groups were synthesized, and their catalytic behavior shows significantly enhanced selectivity and conversion over homogeneous or mixed homogeneous/heterogeneous systems. Current efforts focusing on careful positioning of neighboring thiol and sulfonic acid sites will be reported in due course.

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Supporting information

The online version of this article contains additional supporting information: representative HPLC trace; adsorption/desorption isotherm; XRD analysis; conversion versus selectivity plots.

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