Chapter 3

THIOL/ARYLSULFONIC ACID-PAIRED CATALYSTS FOR THE SYNTHESIS OF BISPHENOLS

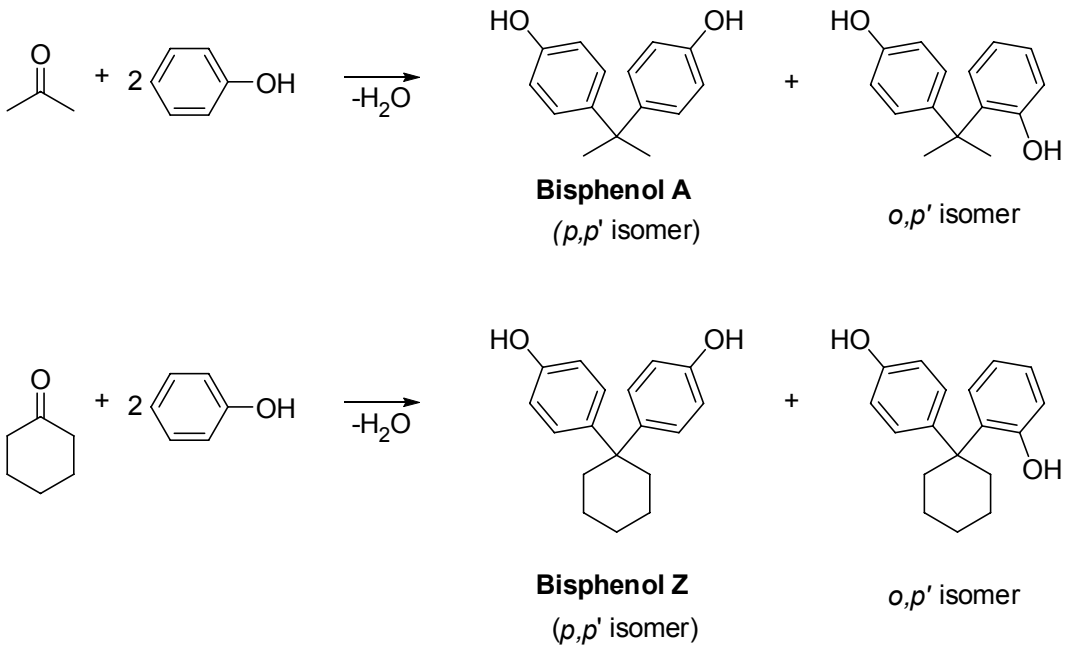
Abstract

We recently demonstrated that mesoporous silica materials functionalized with pairs of alkylsulfonic acid and thiol groups are excellent catalysts for the synthesis of bisphenols from the condensation of phenol and various ketones, with activity and selectivity highly dependent on the thiol/acid distance. Here, we report the synthesis and catalytic properties of a mesoporous silica bearing thiol groups paired with stronger arylsulfonic acid groups. This catalyst was generated by grafting a bissilane precursor molecule containing both a disulfide and a sulfonate ester bond onto SBA-15, followed by simultaneous disulfide reduction and sulfonate ester hydrolysis. The resulting catalyst significantly outperformed the alkylsulfonic acid/thiol paired catalyst in bisphenol A and Z synthesis, while maintaining a very high selectivity to the desired isomer *p,p*' isomer. The paired catalyst had similar activity to a randomly-bifunctionalized arylsulfonic acid/thiol catalyst in the bisphenol A reaction, but exhibited greater activity and selectivity than the randomly-bifunctionalized catalyst in the bisphenol Z reaction.

Introduction

Bisphenols, such as bisphenol A and bisphenol Z, are important industrial feedstocks, especially as monomers in polycarbonate polymers and resins. They are synthesized in the acid-catalyzed condensation between a ketone and phenol, yielding the desired *p,p*' isomer and a byproduct, the *o,p*' isomer (Scheme 3.1). The addition of thiols as a cocatalyst is known to improve both the rate of reaction and the selectivity to the desired isomer.

Mineral acids can be used to catalyze the bisphenol condensation reaction, but solid acid catalysts such as polymeric ion-exchange resins are typically used for commercial bisphenol production due to their non-corrosive nature and reusability. Thiols can be added either as a homogeneous feed additive or as a tethered surface species (thus avoiding product contamination with extremely malodorous thiols). Several solid catalysts bearing both acid and thiol groups attached to a solid support have been reported. Thiols have been covalently tethered to sulfonic acid-containing resins,[1, 2] and polysiloxane catalysts containing randomly alkylsulfonic acid and alkylthiol groups have also been reported to have good catalytic activity for bisphenol A.[3] Zeidan et al.[4] functionalized a mesoporous silica (SBA-15) with arylsulfonic acid and alkylthiol groups and found that the resulting catalyst exhibited good performance only when the acid and thiol groups were in close proximity on the surface (a physical mixture of acid- and thiol-containing materials gave poor results). This observation led us to design SBA-15 catalysts functionalized with discrete alkylsulfonic acid/thiol pairs, and the activity and selectivity of these catalysts was shown to increase markedly as the acid/thiol distance decreased.[5]

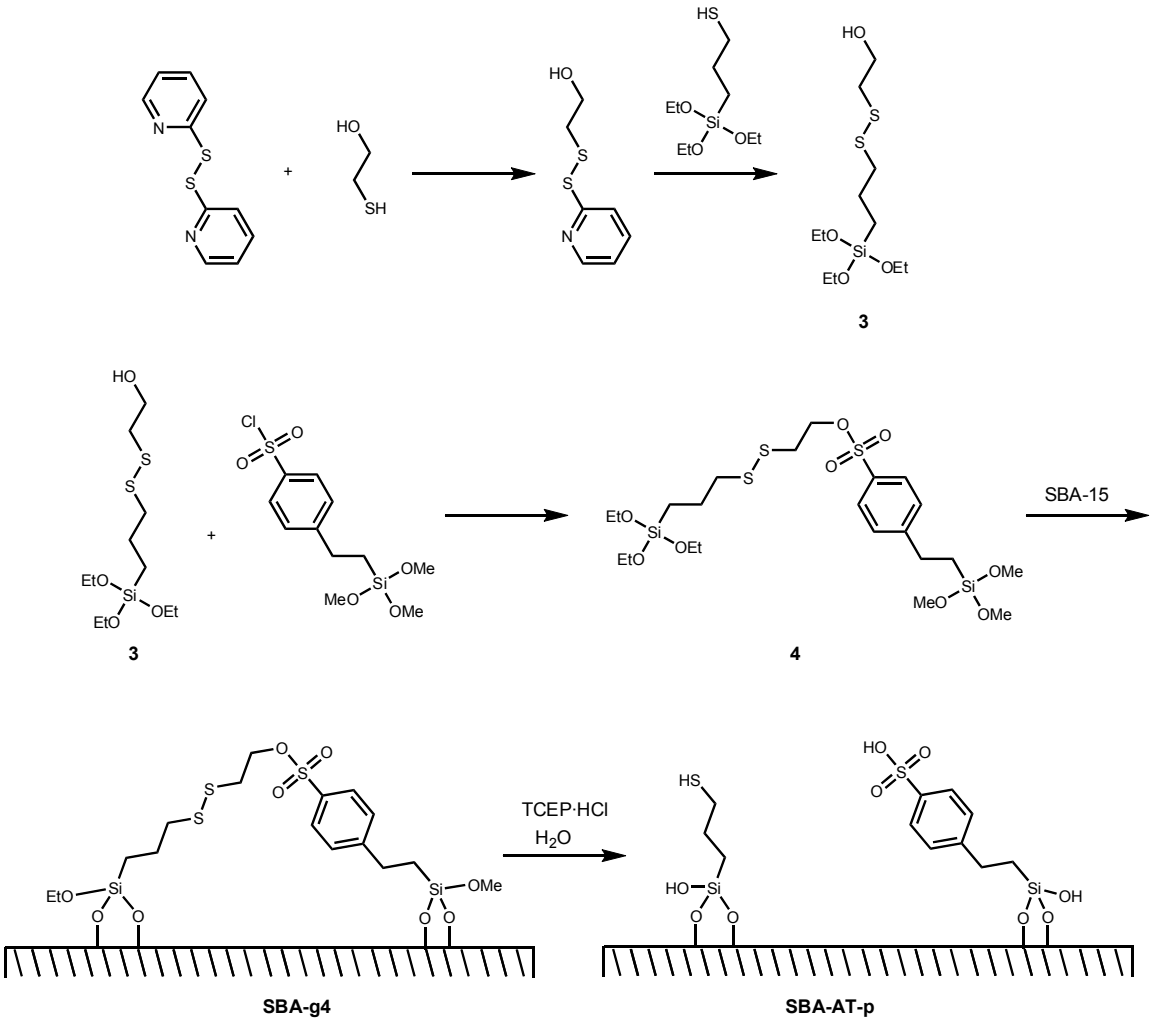


Scheme 3.1. Synthesis of bisphenol A (top) and bisphenol Z (bottom) from phenol and either acetone or cyclohexanone

As a further improvement upon these acid/thiol catalysts, we sought to increase the catalyst activity by increasing the strength of the acid sites. Aromatic sulfonic acids are stronger than alkylsulfonic acids, due to the delocalized pi system of the aryl ring which stabilizes the negative charge of the deprotonated acid. The difference in acidity between aryl- and alkylsulfonic acid-functionalized SBA-15 has been estimated at about 0.2 pK_a units.[6]

To generate arylsulfonic acid/thiol pairs, the bissilane precursor **4** was synthesized, containing both a disulfide group and an aryl sulfonate ester separated by two carbon atoms (Scheme 3.2). After this precursor is grafted onto the silica surface, reduction of the disulfide bond and hydrolysis of the sulfonate ester affords a thiol and arylsulfonic acid group, respectively, in close proximity on the silica surface. This

material was used to catalyze the condensation between phenol and either acetone or cyclohexanone.



Scheme 3.2. Synthesis of disulfide silane **3** (top) and bissilane **4** (middle) and the grafting of **4** onto SBA-15 to generate disulfide/sulfonate ester-functionalized silica **SBA-g4** (bottom), the mercaptoethanol linker of which is cleaved to generate the acid/thiol-paired material **SBA-AT-p**

Results and Discussion

SBA-15 was functionalized with bissilane **4** (the synthesis of which is summarized in Scheme 3.2) by grafting in refluxing toluene. The resulting material is denoted **SBA-g4**. The loading was deliberately kept very low so that the effect of pairing could be seen, and the loading used was ~ 0.2 mmol/g (the same loading as our previously reported alkylsulfonic acid/thiol paired catalyst).[5] SBA-15 was chosen as a support because of its high surface area, regular pore structure, and ease of functionalization.

SBA-g4 was characterized by $^{29}Si\{^{1}H\}$ and $^{13}C\{^{1}H\}$ cross-polarization/magic-angle spinning (CP/MAS) NMR. The tertiary silicon peaks in the ^{29}Si CP/MAS spectrum confirm the presence of covalently bonded organic groups (Figure 3.1, top). T^1, T^2, and T^3 peaks can be seen, corresponding to organosilanes grafted to the surface at one, two, and three points, respectively. Of these three peaks, the largest is T^2, indicating that most of the grafted silanes are covalently bonded to the surface at two points, as shown in Scheme 3.2. Because **4** contains two trialkoxysilane groups, it is possible that one end could graft to the silica surface leaving the other end free. This would be evidenced by a T^0 peak in the ^{29}Si spectrum at -41 ppm, but since no such peak is seen, it appears that nearly every precursor molecule is grafted to the surface at both ends. The ^{13}C CP/MAS spectrum of the grafted molecule corresponds exactly to the solution-phase spectrum of **4**, confirming that the molecule remains intact upon grafting (see Figure 3.2).

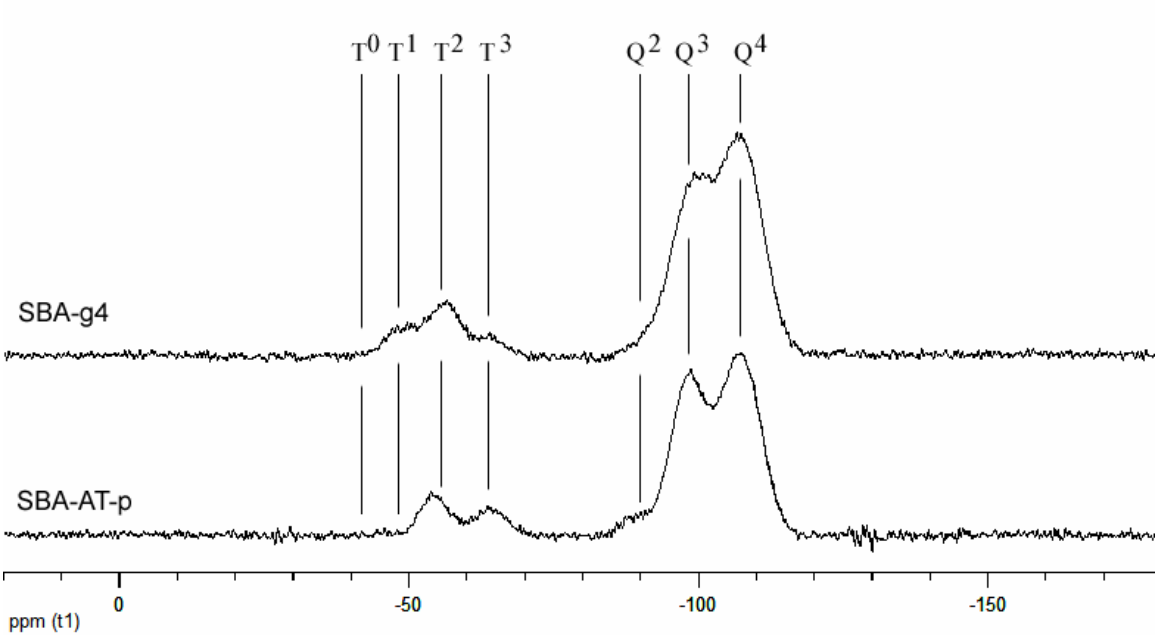


Figure 3.1. The $^{29}Si\{^{1}H\}$ CP/MAS spectrum of **SBA-g4** (top) shows T^1, T^2, and T^3 peaks corresponding to silanes covalently bonded to the surface at one, two, and three points, respectively. The absence of a T^0 peak at -41 ppm indicates that every grafted bissilane is attached to the surface at both ends. Following the cleavage of the mercaptoalcohol linker to form **SBA-AT-p** (bottom) the T^3 peak is larger, the T^2 peak is shifted slightly downfield, and the T^1 peak is nearly absent.

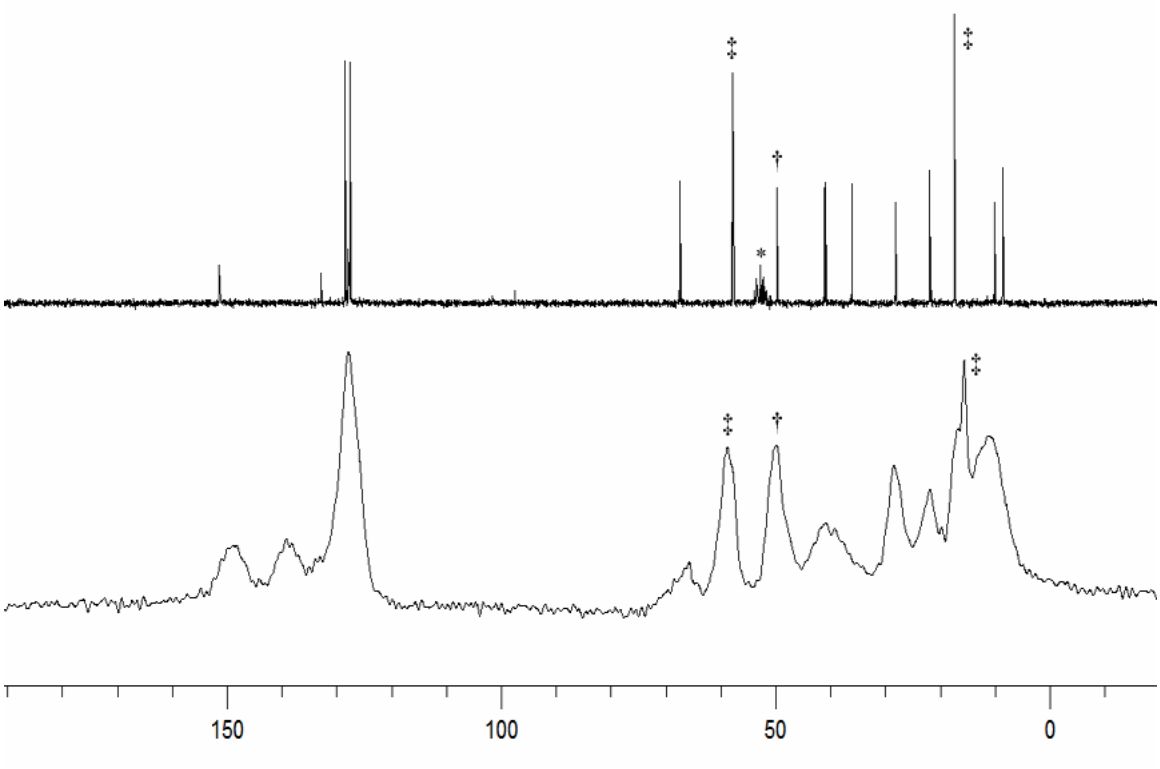


Figure 3.2. The ^{13}C NMR spectrum of bissilane **4** (top) and $^{13}C\{^{1}H\}$ CP/MAS spectrum of **SBA-g4** (bottom) confirm that the disulfide/sulfonate ester structure remains intact following the grafting reaction.

* indicates solvent peak (DMSO-d_6)
‡ indicates ethoxysilyl peaks
† indicates methoxysilyl peaks

The deprotection of the thiols and sulfonic acids of **SBA-g4** was accomplished in one step using aqueous tris(2-carboxyethyl)phosphine hydrochloride (TCEP·HCl). The phosphine reduces the disulfide to a thiol[7] and the weakly acidic aqueous solution hydrolyzes the sulfonate ester to a sulfonic acid. The mercaptoalcohol linker is then free to diffuse away from the acid/thiol site. The resulting deprotected material is denoted **SBA-AT-p** (for Acid/Thiol-paired; capital letters are used here to distinguish these

arylsulfonic acid/thiol materials from the alkylsulfonic acid/thiol materials discussed in the previous chapter).

The ^{13}C CP/MAS spectrum of **SBA-AT-p** is shown in Figure 3.3b. The peaks corresponding to the mercaptoethanol linker (37 and 68 ppm) are absent, confirming that the deprotection step is complete. The residual alkoxy peaks are also absent, as these groups are also hydrolyzed during the aqueous reaction. The ^{29}Si CP/MAS spectrum (Figure 3.1, bottom) shows an increase in the T^3 signal and a decrease in the T^1 signal; thus the aqueous deprotection reaction appears to further condense the alkoxysilane moieties with the surface.*

Nitrogen adsorption/desorption was used to measure the surface area and pore size distribution of these mesoporous materials (see Table 3.1). The unfunctionalized SBA-15 has a surface area of 860 m^2/g. After being grafted with the large bissilane **4**, the surface area drops to 230 m^2/g, and the pore size decreases from 6.3 to 5.8 nm. After the mercaptoethanol linker is removed, the surface area increases to 428 m^2/g and the pore diameter increases to 6.0 nm. Adsorption/desorption isotherms are shown in Figure 3.7 at the end of this chapter.

Acid content was measured by ion-exchange with NaCl, followed by titration of the HCl with NaOH. Thiol content was measured by reaction with Ellman's reagent followed by spectrophotometric quantification of the liberated 2-nitro-5-mercaptobenzoate. The acid/thiol ratio was nearly unity as expected (0.21 mmol/g acid, 0.19 mmol/g thiol), but the total loading was significantly lower than might be expected based on the amount of organosilane used in the grafting reaction (0.7 mmol **4**/g SBA-

* The same phenomenon was noted by Dufaud et al.[8] for a similar aqueous TCEP treatment of organic-functionalized SBA-15.

15). The grafting efficiency of **4** is thus much lower than 100%. It is also possible that the aqueous deprotection step leads to the loss of some grafted organic groups, leaving some of the acid and thiol groups without a paired counterpart. The catalyst characterization data are summarized in Table 3.1.

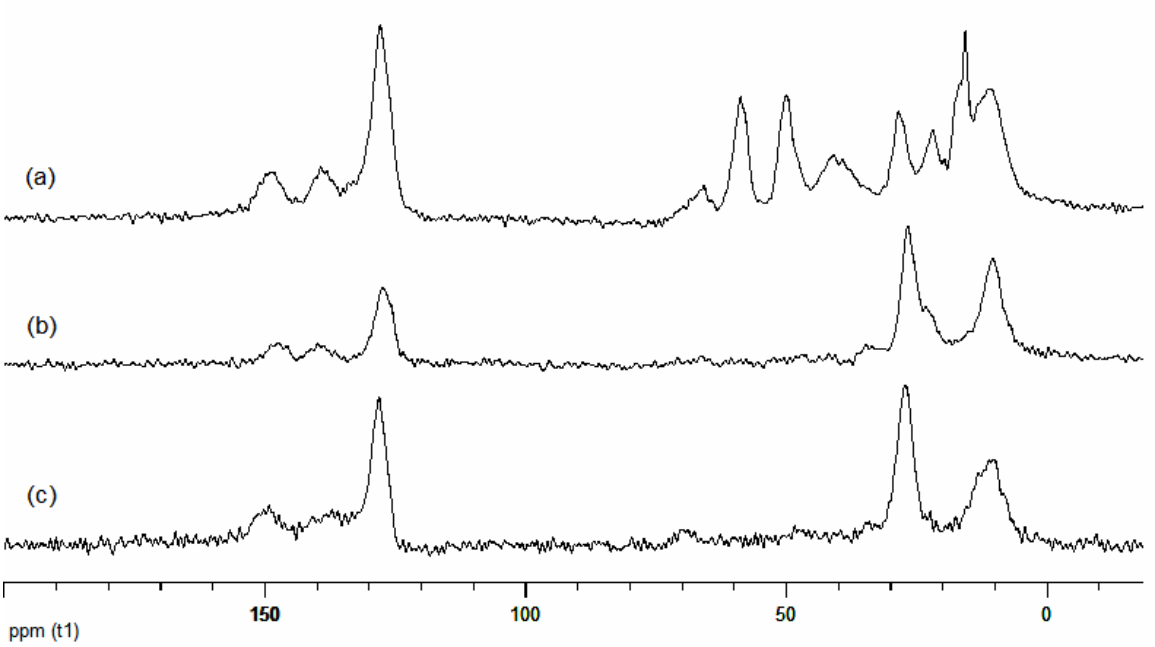
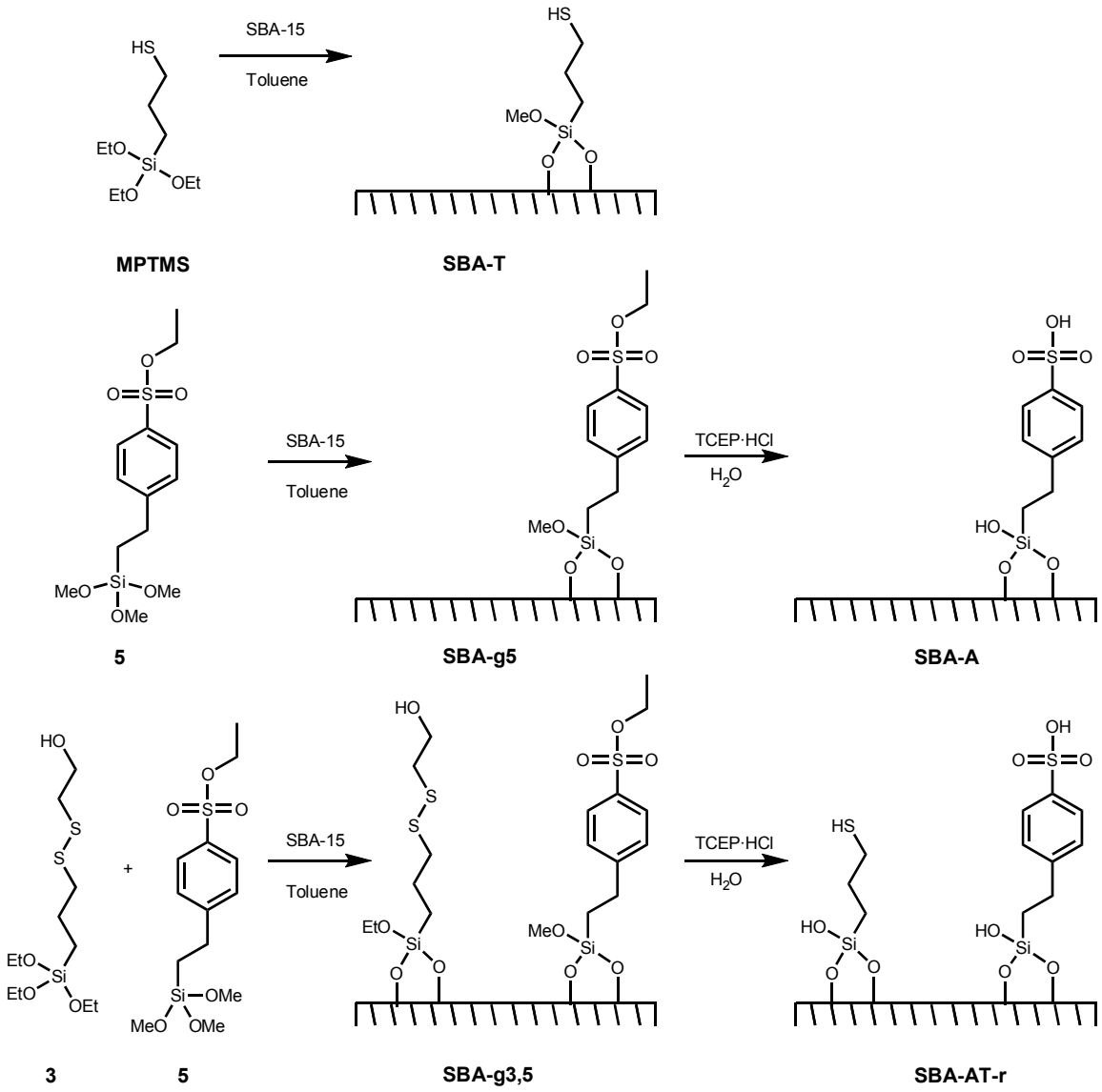


Figure 3.3. $^{13}C\{^{1}H\}$ CP/MAS NMR spectra of (a) **SBA-g4**; (b) **SBA-AT-p**; (c) **SBA-AT-r**

Catalysts containing only thiols, only arylsulfonic acids or randomly-distributed arylsulfonic acid and thiol groups were also synthesized (denoted **SBA-T**, **SBA-A**, and **SBA-AT-r**, respectively) according to Scheme 3.3. The acid groups were generated by sulfonate ester hydrolysis, using the same aqueous TCEP·HCl treatment employed for **SBA-AT-p**. The disulfide silane **3** was used as the source of thiol groups for **SBA-AT-r**, because a free thiol could attack the sulfonate ester during the grafting process. As expected, the ^{13}C NMR spectrum of **SBA-AT-r** is identical to that of **SBA-AT-p** (Figure

3.3c) because the same functional groups are present on the surface of both materials; the only difference is the spatial positioning of these groups.

With these randomly bifunctionalized materials, the thiol/acid ratio is not fixed at unity. Because previous results[4] suggest that a thiol/acid ratio greater than 1 leads to greater activity (per acid site) and selectivity, a randomly-bifunctionalized material with a thiol/acid ratio of 2 was also prepared (denoted **SBA-AT-r2**).



Scheme 3.3. (Top) Grafting 3-mercaptopropyltrimethoxysilane (MPTMS) onto SBA-15 generates **SBA-T**, containing only thiol sites. (Middle) Grafting sulfonate ester precursor **5** generates intermediate **SBA-g5**, which is hydrolyzed to **SBA-A**, containing only acid sites. (Bottom) Grafting both disulfide **3** and sulfonate ester **5** generates intermediate **SBA-g3,5** which is deprotected to form **SBA-AT-r**, containing randomly-distributed acid and thiol sites.

Entry	Material	S_{BET}[a] (m^2/g)	D_p[b] (nm)	H^+[c] (mmol/g)	SH[d] (mmol/g)	SH/H^+
1	**SBA-15**	860	6.3			
2	**SBA-g4**	230	5.8			
3	**SBA-A**			0.20		
4	**SBA-AT-p**	428	6.0	0.21	0.19	0.9
5	**SBA-AT-r**			0.13	0.12	0.9
6	**SBA-AT-r2**			0.06	0.13	2.2
7	**SBA-T**				0.32	

Table 3.1. Catalyst characterization data

[a] Specific surface area, calculated using BET method
[b] Average pore diameter, calculated from adsorption isotherm using BJH method
[c] Acid loading, measured by ion exchange/titration
[d] Thiol loading, measured by reaction with Ellman's reagent

Catalytic Reactions

The above materials were used to catalyze the synthesis of bisphenol A (see Table 3.2). **SBA-T** was almost completely inactive due to its lack of acid sites (Entry 1). **SBA-A** exhibited some catalytic activity, but very low selectivity due to its lack of thiol sites (Entry 2). When a physical mixture of these two catalysts was employed (Entry 3), the activity and selectivity improved only slightly beyond that for **SBA-A** alone, because the acid and thiol groups are spatially isolated and unable to interact except at the outer surfaces of the particles. When a homogeneous acid, *para*-toluenesulfonic acid (pTSA) was used, the activity was very close to that of **SBA-A**, albeit with an even lower selectivity (Entry 4). When pTSA and **SBA-T** were used together (Entry 5) the activity and selectivity were improved somewhat, as the acid was able to enter the silica pores and interact with the surface-bound thiols. The catalysts containing both acid and thiol sites in close proximity on the same silica support exhibited very high activity (total yield of 113–133 per acid site; see Entries 6–8) and good selectivity to the desired *p*,*p*' isomer.

Among the heterogeneous acid/thiol catalysts, the randomly-bifunctionalized catalyst **SBA-AT-r2** with a 2:1 thiol/acid ratio (Entry 7) gave the highest catalytic activity, with a per-site yield of 133. The 1:1 thiol/acid materials exhibited very similar activity despite the difference in the spatial positioning of the acid and thiol groups. The paired catalyst was the most selective (isomer ratio of 19.3) but was no more active than the random 1:1 catalyst. Compared to the alkylsulfonic acid-containing catalysts **SBA-a** and **SBA-at-p** discussed in the previous chapter (Entries 9–10) it is clear that the greater acid strength of the arylsulfonic acid groups leads to greater overall activity without sacrificing selectivity.

Entry	Catalyst(s)	Thiol/Acid Ratio	PER-SITE YIELD *p*,*p*'	*o*,*p*'	Total	Isomer Ratio
1	**SBA-T**[a]		<0.1	<0.1	<0.2	
2	**SBA-A**		23	11	34	2.1
3	**SBA-A** + **SBA-T**	1	28	11	39	2.6
4	pTSA		21	13	34	1.6
5	pTSA + **SBA-T**	1	35	12	47	2.9
6	**SBA-AT-r**	1	106	7	113	15.2
7	**SBA-AT-r2**	2	125	8	133	15.6
8	**SBA-AT-p**	1	108	6	114	19.3
9	**SBA-a**[b]		2	1.1	3.1	1.8
10	**SBA-at-p**[b]	1	78	5.6	83	14.0

Table 3.2. Catalytic data for bisphenol A synthesis. Reaction conditions: 0.02 mmol H^+, 6 mmol acetone, 24 mmol phenol, 90°C, 24 hr. Per-site yield calculated as mmol product/mmol H^+

[a] 0.02 mmol SH was used; per-site yield calculated on basis of thiol sites instead of acid sites.
[b] Data taken from Ref 5 (see previous chapter).

The heterogeneous acid/thiol catalysts were also tested in the condensation of cyclohexanone with phenol to form bisphenol Z. This reaction is slower and has been

previously shown to be more highly sensitive to acid/thiol positioning than the bisphenol A reaction.[5] The catalytic results are shown in Table 3.3.

Entry	Catalyst(s)	Thiol/Acid Ratio	PER-SITE YIELD *p*,*p*'	*o*,*p*'	Total	Isomer Ratio
1	**SBA-T**[a]		0	0	0	
2	**SBA-A**		8.1	3.8	11.9	2.1
3	**SBA-A** + **SBA-T**	1	7.9	3.6	11.4	2.2
4	**SBA-A** + PrSH	1	7.3	4.2	11.5	1.8
5	pTSA		3.2	2.6	5.8	1.2
6	pTSA + **SBA-T**	1	4.5	3.0	7.5	1.5
7	**SBA-AT-r**	1	17	4.0	21	4.3
8	**SBA-AT-p**	1	27	2.0	29	13.6
9	**SBA-a**[b]		0.3	0[c]	0.3	N/A[c]
10	**SBA-at-p**[b]	1	13	0.9	14	14.3

Table 3.3. Catalytic data for bisphenol Z synthesis. Reaction conditions: 0.02 mmol H^+, 6 mmol cyclohexanone, 24 mmol phenol, 90°C, 24 hr. Per-site yield calculated as mmol product/mmol H^+

[a] 0.02 mmol SH was used; per-site yield calculated on basis of thiol sites instead of acid sites.
[b] Data taken from Ref 5 (see previous chapter).
[c] *o*,*p*' isomer below detection limit

The yield of bisphenol Z is 3–6 times lower than that of bisphenol A at the same reaction conditions due to the lower reactivity of the cyclohexanone reactant. **SBA-A** gives a per-site yield of only 11.9 (Entry 2) and no improvement is seen when a physical mixture of **SBA-A** and **SBA-T** is used (Entry 3). Notably, no cooperativity is seen when a homogeneous thiol is used in conjunction with **SBA-A** (Entry 4) and only a minor improvement is seen with the homogeneous acid catalyst when heterogeneous thiol is added (Entries 5–6). Only when the acid and thiol groups are both immobilized on the silica surface does cooperativity become evident. **SBA-AT-r** (Entry 7) has a yield (21) and selectivity (4.3) approximately twice that of **SBA-A**. Organizing the acid and thiol sites into pairs (Entry 8) further increases the yield to 29 and imparts a very high

selectivity (13.6). Compared to the alkylsulfonic acid-containing catalyst **SBA-at-p** (Entry 10) the arylsulfonic acid/thiol-paired catalyst **SBA-AT-p** is twice as active, while retaining the same high selectivity.

These data demonstrate that catalytic cooperativity in the synthesis of bisphenol Z is much more dependent on acid/thiol distance than for bisphenol A. Combining a homogeneous acid with a heterogeneous thiol (or vice versa) does not provide the necessary proximity for good catalytic activity because the homogeneous component is dispersed throughout the liquid phase. Immobilizing both the acid and thiol onto silica fixes the groups on the two-dimensional surface, leading to greater proximity and catalytic performance. Finally, organizing the acid and thiol groups into closely spaced surface pairs leads to a further improvement in activity and a dramatic increase in selectivity that is not seen in the bisphenol A reaction.

Conclusions

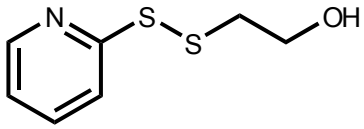
A mesoporous silica catalyst featuring arylsulfonic acid and alkylthiol groups organized in pairs was synthesized by grafting a bissilane precursor onto SBA-15, followed by linker cleavage. Compared to catalysts containing weaker alkylsulfonic acid sites, the arylsulfonic acid catalysts are more active while maintaining similar selectivities. In the bisphenol A reaction, the random and paired arylsulfonic acid/thiol catalysts exhibit similar catalytic performance, whereas in the slower bisphenol Z reaction the paired catalyst outperforms the randomly-distributed catalyst.

The acid/thiol distance in **SBA-AT-p** was set by the mercaptoethanol spacer used in the precursor. Other mercaptoalcohol linkers could be used, allowing for the acid/thiol

distance to be tuned. Replacing the alkyl spacer (which is somewhat flexible) with a more rigid one might also lead to a greater uniformity in acid/thiol distance. This fine-tuning of acid/thiol distance would be expected to be especially important for even slower bisphenol condensations, and could potentially catalyze the condensation of phenol with less-reactive ketones without requiring very high reaction temperatures, and potentially opening the door for the development of new bisphenol-based materials.

Experimental

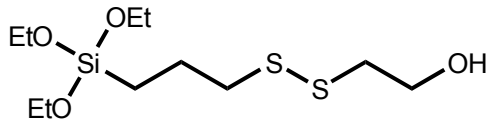
Materials. Dichloromethane, pentane, and toluene were dried by distillation over CaH_2, $CaSO_4$, and Na respectively and stored over activated 4 Å molecular sieves. All other solvents were analytical grade and used as received. Tris(2-carboxyethyl)phosphine hydrochloride was purchased from Alfa Aesar. Tetraethoxysilane (TEOS), 2-mercaptoethanol and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (50% in dichloromethane) were obtained from Acros Organics. 3-Mercaptopropyltriethoxysilane was purchased from Gelest. All other chemicals were purchased from Aldrich and used as received. All reactions were performed under an argon atmosphere.



2-(Pyridin-2-yldisulfanyl)ethanol. A solution of 2-mercaptoethanol (0.87 g, 11.1 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise at room temperature to a solution of 2,2'-dithiopyridine (4.89 g, 22.2 mmol) in CH_2Cl_2 (20 mL). After complete addition of the mercaptoethanol, the solution was stirred for three hours at room temperature. The

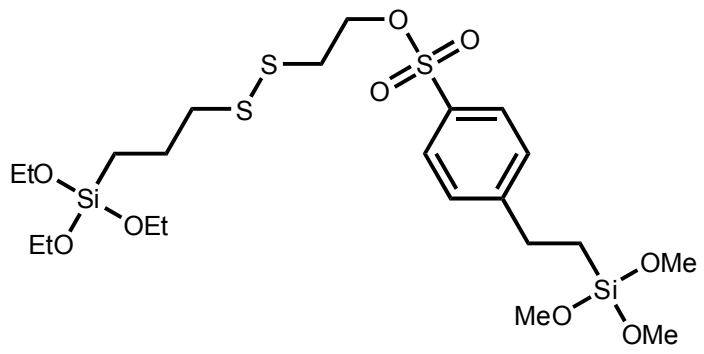
initially colorless solution turned yellow due to the production of pyridine-2-thione. After the solvent was removed *in vacuo*, chromatography on silica gel (8:2 pentane/ethyl acetate) afforded 2-(pyridin-2-yldisulfanyl)ethanol (1.4 g, 68% yield) as a yellow oil.

^{1}H NMR, $CDCl_3$, δ 2.71 ppm (t, 2H, $C_5H_4NS_2$*CH_2*CH_2OH), 3.59 ppm (q, 2H, $SSCH_2$*CH_2*OH), 5.5 ppm (t, 1H, $SSCH_2CH_2$*OH*), 6.89, 7.33, 8.2 ppm (m, 4H, pyridyl); ^{13}C NMR, $CDCl_3$, δ 42.1 ppm ($SSCH_2CH_2OH$), 58.9 ppm ($SSCH_2CH_2OH$), 120.9, 121.3, 137.1, 149.2, and 159.2 ppm (pyridyl carbons).



2-((3-(triethoxysilyl)propyl)disulfanyl)ethanol (Organosilane 3). A solution of 3-mercaptopropyltriethoxysilane (1.61 g, 6.74 mmol) in dry CH_2Cl_2 (10 mL) was added slowly via syringe to a solution of 2-(pyridin-2-yldisulfanyl)ethanol (1.40 g, 7.49 mmol) in CH_2Cl_2 (20 mL). The yellow solution was stirred at room temperature overnight. The crude product was purified by chromatography on silica gel (6:4 cyclohexane/ethyl acetate) to afford **3** (1.27 g, 60% yield).

^{1}H NMR, $CDCl_3$, δ 0.6 ppm (m, 2H, $SiCH_2CH_2$), 1.1 ppm (t, 9H, $SiOCH_2CH_3$), 1.6 ppm (m, 2H, $SiCH_2CH_2$), 2.6 ppm (t, 2H, $SSCH_2CH_2CH_2$), 2.7 ppm (t, 2H, $HOCH_2CH_2SS$), 3.4 ppm (br, 1H, O*H*), 3.7 ppm (q, 8H, $SiOCH_2CH_3$ and $HOCH_2CH_2SS$); ^{13}C NMR, $CDCl_3$, δ 9.2 ppm ($SiCH_2CH_2$), 17.7 ppm ($SiOCH_2CH_3$), 22.4 ppm ($SSCH_2CH_2CH_2$), 40.9 ppm ($SSCH_2CH_2CH_2$), 41.5 ppm ($HOCH_2CH_2SS$), 58.3 ppm ($SiOCH_2CH_3$), 60.3 ppm ($HOCH_2CH_2SS$).

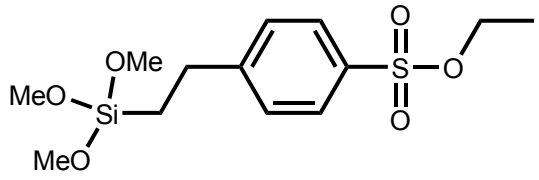


2-((3-(triethoxysilyl)propyl)disulfanyl)ethyl 4-(2-(trimethoxysilyl)ethyl) benzenesulfonate (Bissilane 4). A solution of **3** (1.23 g, 3.93 mmol) and dry triethylamine (1.02 g, 10.1 mmol) in dry CH_2Cl_2 (20 mL) was cooled to 0°C and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (50% in CH_2Cl_2, 1.4 mL, 2.8 mmol) was added dropwise via syringe. The mixture was allowed slowly to warm to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the crude product was purified by chromatography on tetramethylorthosilicate-passivated silica gel (6:4 CH_2Cl_2/ethyl acetate) to afford **4** (0.67 g, 40% yield).

^{1}H NMR, CD_2Cl_2, δ 0.7 ppm (m, 2H, Si*CH*$_2$CH$_2$CH$_2$), 1.0 ppm (m, 2H, Si*CH*$_2$CH$_2$), 1.2 ppm (t, 9H, SiOCH$_2$*CH*$_3$), 1.8 ppm (m, 2H, SiCH$_2$*CH*$_2$CH$_2$), 2.7 ppm (t, 2H, SiCH$_2$*CH*$_2$), 2.8 ppm (m, 4H, SO$_2$OCH$_2$*CH*$_2$SS and SiCH$_2$CH$_2$*CH*$_2$), 3.6 ppm (s, 9H, SiO*CH*$_3$), 3.8 ppm (q, 6H, SiO*CH*$_2$CH$_3$), 4.3 ppm (t, 2H, SO$_2$O*CH*$_2$CH$_2$SS), 7.4 ppm (d, 2H, phenyl proton β to ethyl chain), 7.8 ppm (d, 2H, phenyl proton β to sulfonate ester group).

^{13}C NMR, CD_2Cl_2, δ 9.2 ppm (Si*CH*$_2$CH$_2$CH$_2$), 10.7 ppm (Si*CH*$_2$CH$_2$), 17.7 ppm (SiOCH$_2$*CH*$_3$), 22.5 ppm (SiCH$_2$*CH*$_2$CH$_2$), 28.8 ppm (SiCH$_2$*CH*$_2$), 36.6 ppm (SO$_2$OCH$_2$*CH*$_2$SS), 41.6 ppm (SiCH$_2$CH$_2$*CH*$_2$), 50.3 ppm (SiO*CH*$_3$), 58.2 ppm (SiO*CH*$_2$CH$_3$), 68.0 ppm (SO$_2$O*CH*$_2$CH$_2$SS), 127.8 and 128.8 ppm (aromatic carbons),

133.0 ppm (aromatic carbon attached to ethyl group), 151.4 ppm (aromatic carbon attached to sulfonate ester).



Ethyl 4-(2-(trimethoxysilyl)ethyl)benzenesulfonate (Organosilane 5). 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (50% in dichloromethane, 1.9 mL, 3.8 mmol) was added dropwise through a septum to a solution of dry ethanol (0.88 g, 19 mmol) and triethylamine (1.56 g, 15.4 mmol) at 0°C. After the addition, the mixture was allowed slowly to warm at room temperature. The reaction mixture was stirred at 25°C overnight. After the solvent was removed *in vacuo*, filtration on silica gel (ethyl acetate) afford **5** (0.5 g, 40% yield).

^{1}H NMR, $CDCl_3$, δ 0.9 ppm (m, 2H, Si*CH*$_2$CH$_2$), 1.21 ppm (t, 3H, *CH*$_3$CH$_2$O), 2.74 ppm (m, 2H, C$_6$H$_4$*CH*$_2$), 3.5 ppm (s, 9H, SiO*CH*$_3$), 4.0 ppm (q, 2H, CH$_3$*CH*$_2$O), 7.33 ppm (d, 2H, phenyl protons β to ethyl chain), 7.7 ppm (d, 2H, phenyl protons β to sulfonate ester group). ^{13}C {^{1}H} NMR, $CDCl_3$, δ 10.8 (Si*C*H$_2$CH$_2$) ppm, 14.6 ppm (*C*H$_3$CH$_2$O), 28.7 ppm (C$_6$H$_4$*C*H$_2$), 50.4 ppm (SiO*C*H$_3$), 66.8 ppm (CH$_3$*C*H$_2$O), 127.8 and 128.8 ppm (aromatic carbons), 133.0 ppm (aromatic carbon attached to ethyl group), 150.8 ppm (aromatic carbon attached to sulfonate group).

Organic-functionalized SBA-15 materials. SBA-15 (1.0 g, synthesized according to the literature procedure[9, 10]) was suspended in dry toluene (40 mL). A solution of organosilane in toluene (10 mL) was added dropwise via syringe. The suspension was stirred for 2 hours at room temperature, then refluxed overnight. After cooling to room

temperature, the solids were filtered and washed several times with toluene and dried under high vacuum.

When two organosilanes were grafted onto the same SBA-15 material, two separate solutions of organosilane in toluene were prepared and were added dropwise simultaneously to the SBA-15 suspension.

Surface Disulfide Reduction and Sulfonate Ester Hydrolysis. Functionalized silica (0.5 g) containing disulfide and/or sulfonate ester surface groups was suspended in an aqueous solution of TCEP·HCl (16 mM, 50 mL) and stirred at 50°C for 48 hours. After filtration, the solids were washed with water (5 x 100 mL), then suspended in 0.5 N HCl for ~ 1 hour to acidify, followed by washing with water (5 x 100 mL). The material was then dried under high vacuum.

Quantification of Acid Sites. Acid-containing silica (40 mg) and 2N aqueous NaCl (4 mL) were stirred at room temperature for 24 hours. The solids were filtered off using positive air pressure filtration and were washed with water (4 x 2 mL). The combined filtrate was titrated with 0.01N NaOH using phenol red as indicator.

Quantification of Thiol Sites. We followed the procedure developed by Badyal et al.[11] for quantification of resin-bound thiols in organic solvents. Thiol-containing silica (5 mg) was suspended in methanol (4 mL) and 1 mL of a solution containing Ellman's reagent (4 mg/mL) and diisopropyl ethylamine (0.05mL/mL) was added. After stirring at room temperature for 4 hours, the solids were removed by syringe-filtration and the absorbance of the filtrated was measured at 412 nm, using an experimentally determined exctinction coefficient of 11 mM^{-1}.

Catalytic Reaction—Condensation of Phenol and Ketone. An amount of catalyst corresponding to 0.02 mmol H^+ (~ 100–200 mg) was added to a vial and dried under high vacuum at 80°C overnight. Phenol (2.2 g, 24 mmol) and ketone (6 mmol) were added and the vial was sealed under argon and stirred at 90°C for 24 hours. The catalyst was removed by filtration and washed with acetonitrile to a total filtrate volume of 25 mL, and the products were quantified by HPLC analysis. Per-site yield was calculated on the basis of the number of acid sites present and selectivity was defined as the ratio of bisphenol isomers (*p,p*'/*o,p*').

When homogeneous catalysts were used, the homogeneous catalyst was dissolved in the ketone and then added to the phenol and heterogeneous catalyst.

Acknowledgements

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Additional Figures

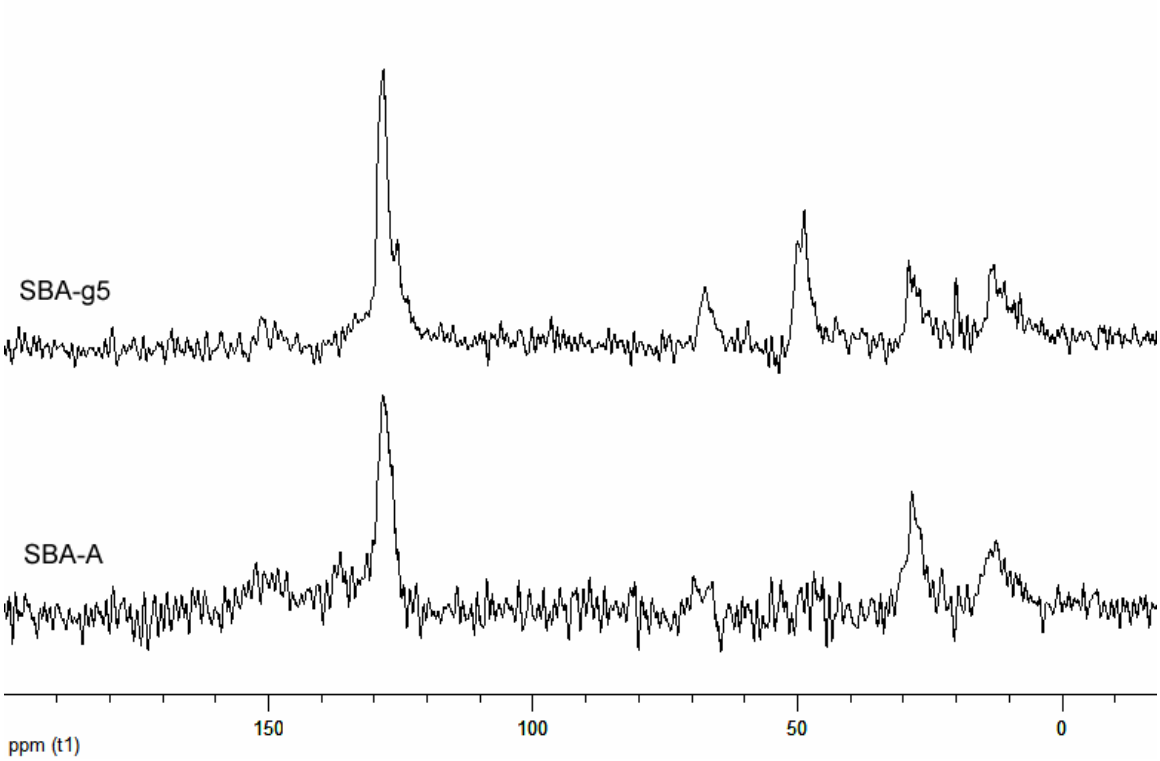


Figure 3.4. $^{13}C\{^{1}H\}$ CP/MAS NMR spectra of **SBA-g5** (top) and **SBA-A** (bottom). The peak at 67 ppm is due to the ethyl ester and is nearly absent in **SBA-A**. The small peak in the **SBA-g5** spectrum at 21 ppm is due to residual adsorbed toluene.

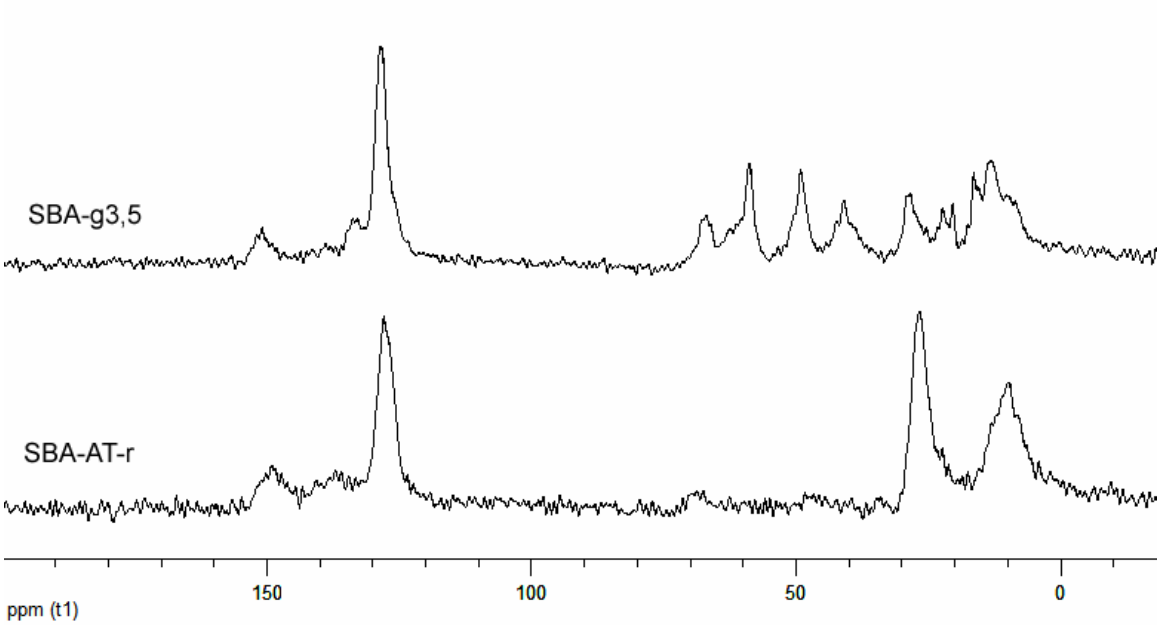


Figure 3.5. $^{13}C\{^{1}H\}$ CP/MAS NMR spectra of **SBA-g3,5** (top) and **SBA-AT-r** (bottom). The ethyl ester peak (67 ppm) and mercaptoethanol peaks (41 ppm, 60 ppm) are absent in **SBA-AT-r** following deprotection. The residual ethoxy (16 ppm, 58 ppm) and methoxy peaks (49 ppm) are also hydrolyzed in the deprotection process. The small peak in the **SBA-g3,5** spectrum at 21 ppm is due to residual adsorbed toluene.

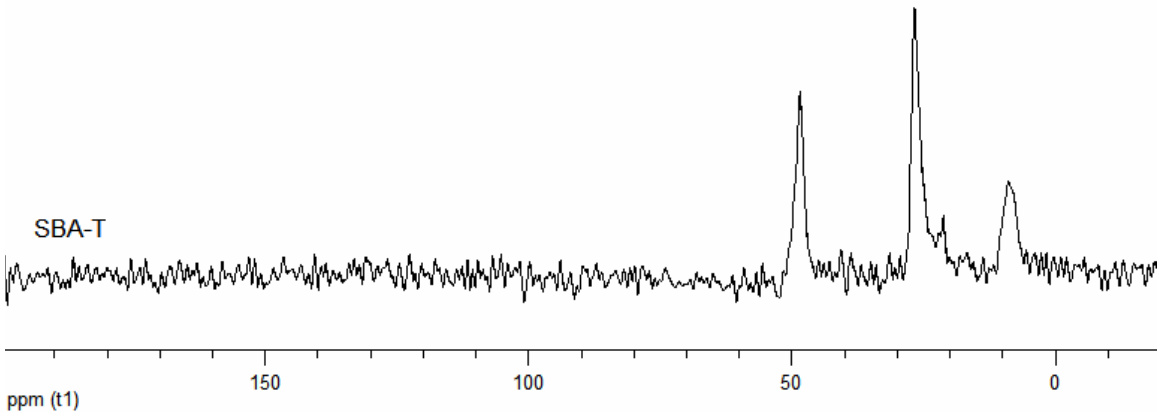
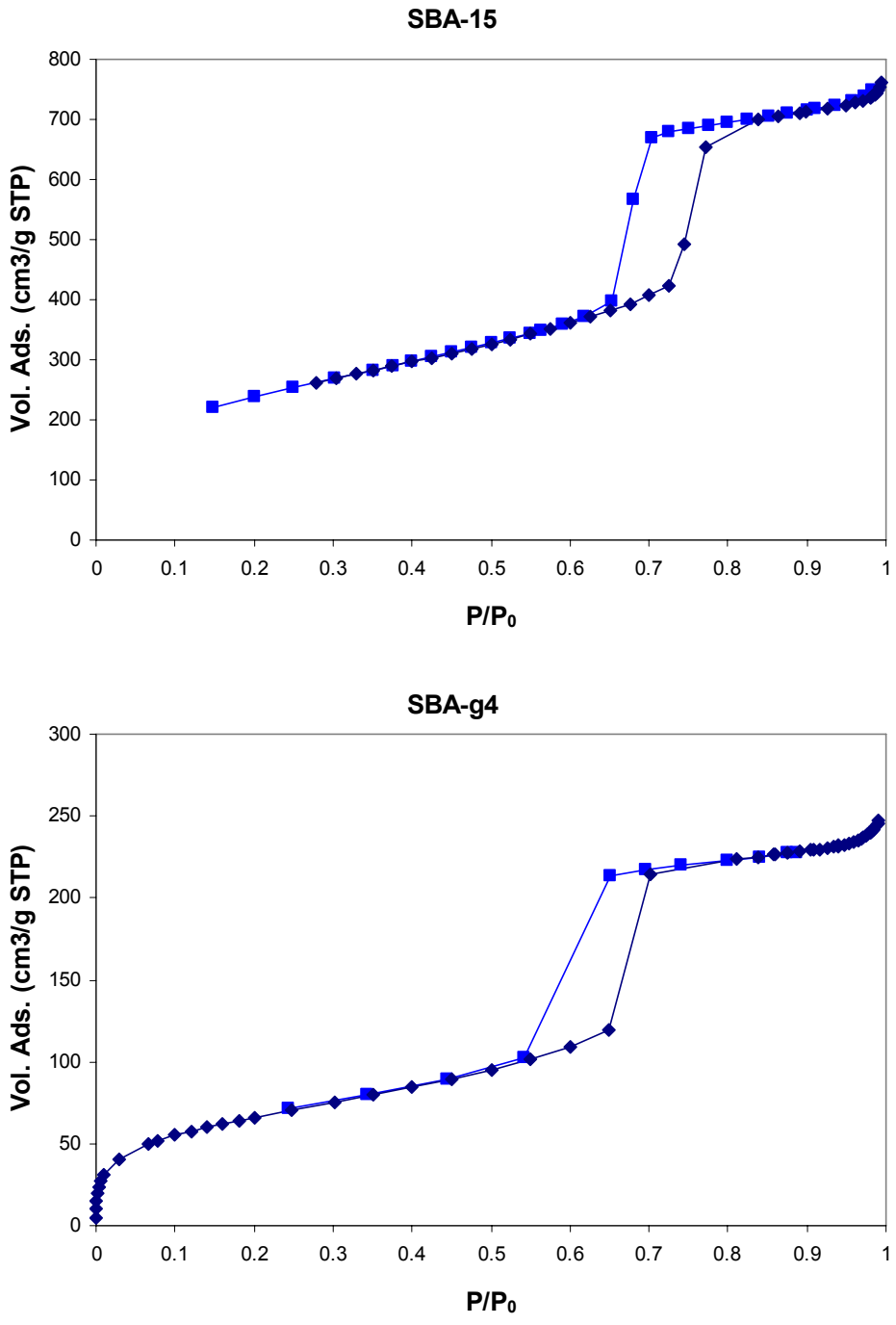
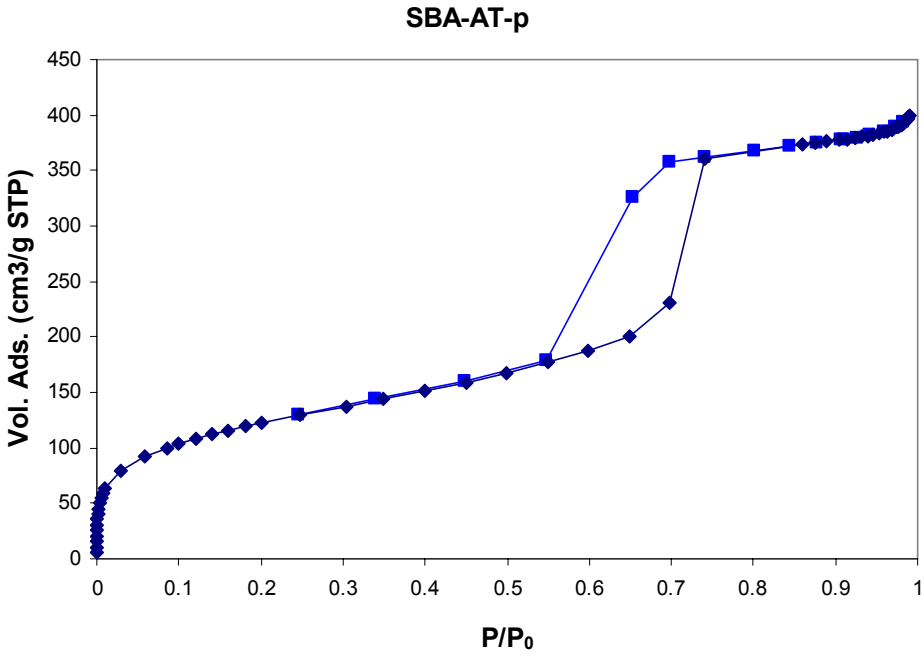


Figure 3.6. $^{13}C\{^{1}H\}$ CP/MAS NMR spectra of **SBA-T**. The peak at 49 ppm is due to residual methoxy groups. The small peak at 21 ppm is due to residual adsorbed toluene.

Figure 3.7. N_2 adsorption/desorption isotherms (diamonds = adsorption branch; squares = desorption branch)




SBA-AT-p
Vol. Ads. (cm3/g STP)
450
400
350
300
250
200
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
P/P0