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Supporting Information For

Aromatic-Hydroxyl Interaction of an alpha-aryl ether Lignin Model-Compound on a Porous Silicate, Present at Pyrolysis Temperatures

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Contents

S1. Peak integrated areas and definitions of the C-H stretching region	2
S2. Peak integrated areas and definitions: comparison of the free Si-OH hydroxyl (~3745 cm⁻¹) and coordinated hydroxyl (~3610 cm⁻¹) regions (for Figure 4 of the main text)	3
S3. Mass spec data	4
S4. Thermogravimetric analysis (TGA) data for BPEa-SBA-15	5
S6. ¹³C NMR Data	7
S6.1 BPE physisorbed on SBA-15 (solid state) (¹³C)	7
S6.2 BPEa-SBA-15 (solid state) (¹³C)	8
S6.3 Pure BPE (solid state) (¹³C)	8
S6.4 Pure BPEa (¹³C CP)	9
S6.5 BPEa-SBA-15 (¹³C CP) before and after heating	9
S7. DRIFTS Spectra of Neat SBA-15 with and without adsorbed water	10
S8. NMR and IR data for physisorbed molecules	11
S8.1 IR data for BPE physisorbed on several silicate surfaces	11
S8.2 NMR data for BPE physisorbed on SBA-15	12
S9. Discussion About Strength of Aromatic-Hydroxyl Bonding Complex	14

S1. Peak integrated areas and definitions of the C-H stretching region

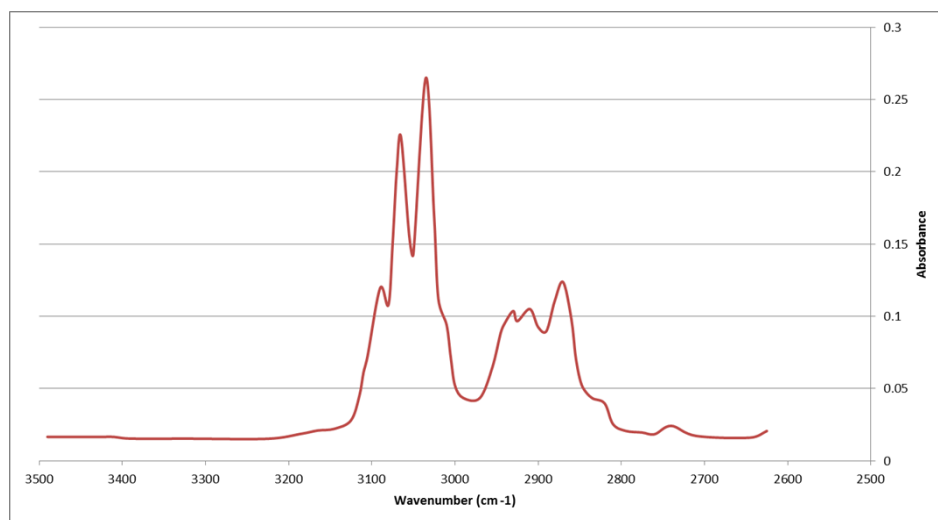
Table S1a. Integrated areas and Peak area ratios for Region I (>3000 cm⁻¹) to Region II (<3000 cm⁻¹) of (BPEa)-SBA-15 after successive heatings and pure BPE

Temperature	Above 3000 cm ⁻¹	Below 3000 cm ⁻¹	Ratio
	Baseline: 3131-2996 Region: 3131-2994	Baseline: 2989-2802 Region: 2991-2796	
70° C before exp.	76.322	85.097	0.897
After 300° C	98.217	76.385	1.286
After 350° C	95.652	93.973	1.02
After 400° C	95.004	22.685*	4.19*
After 600° C	75.312	5.408*	13.9*
BPE gas phase (NIST)	6.399	1.36	4.7
BPE bulk phase (sigma)			2.0

*These values are in fairly significant error due to difficulties in integration, but are still useful for comparison purposes. NIST webbook BPE spectrum: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C946805&Units=SI&Mask=80#IR-Spec>

For the Bulk BPE transmission spectrum obtained from Sigma-Aldrich, the integrated absorbance of Region I to Region II is ~2.0 (see below), while for gas phase BPE this ratio is ~4.7. With bulk BPE on salt-plates obtained in-house, the ratio was also ~1.5 +/- 0.2. For BPEa-SBA-15 the ratio is slightly below 1.0 before heating above 300° C.

Absorbance of bulk phase BPE, digitized from file FTIR006259 obtained from Sigma-aldrich at <http://www.sigmaaldrich.com/spectra/ftir/FTIR006259.PDF>



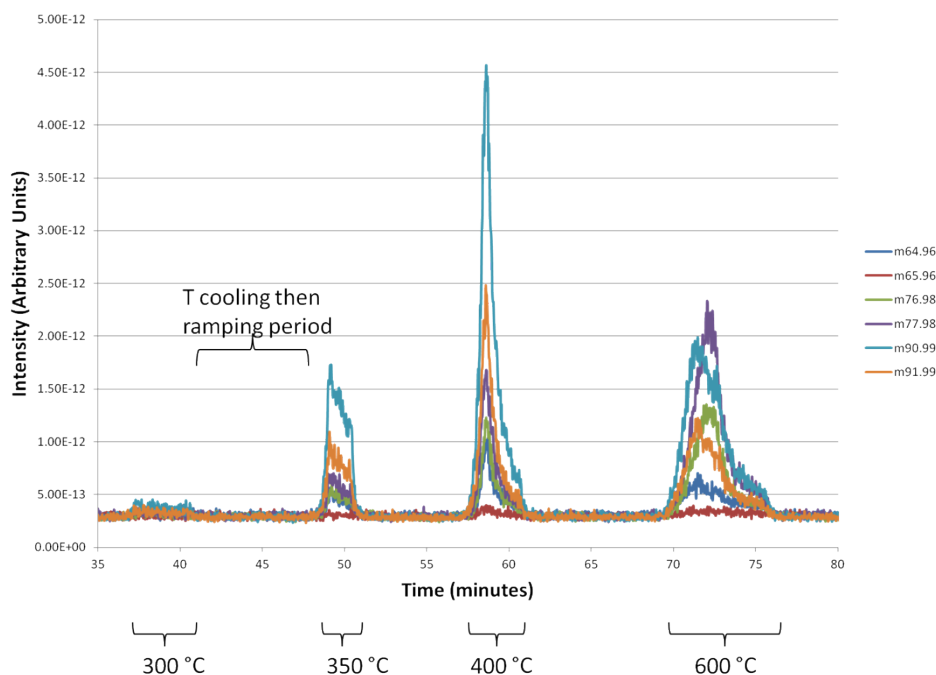
S2. Peak integrated areas and definitions: comparison of the free Si-OH hydroxyl (~3745 cm⁻¹) and coordinated hydroxyl (~3610 cm⁻¹) regions (for Figure 4 of the main text)

Table S2. Integrated Areas and Peak areas for the C-H Region I, C-H Region I, silanol band, and coordinated hydroxyl.

Temperature	C-H Region I Baseline: 3131-2996 Region: 3131-2994	C-H Region II Baseline: 2982-2802 Region: 2991-2796	Silanol (Final minus current times 6.5) Baseline: 3752-3727 Region: 3752-3727	Coordinated hydroxyl (initial minus final, times 2) Baseline: 3704-3563 Region: 3702-3563
70 °C start	76.322	85.097	86.359	71.884
70 °C after 300 °C	98.217	76.385	73.8335	78.326
70 °C after 350 °C	95.652	93.973	68.5555	68.876
70 °C after 400 °C	95.004	22.685	41.093	37.9
70 °C after 600 °C	75.312	5.408	0	0

S3. Mass spec data

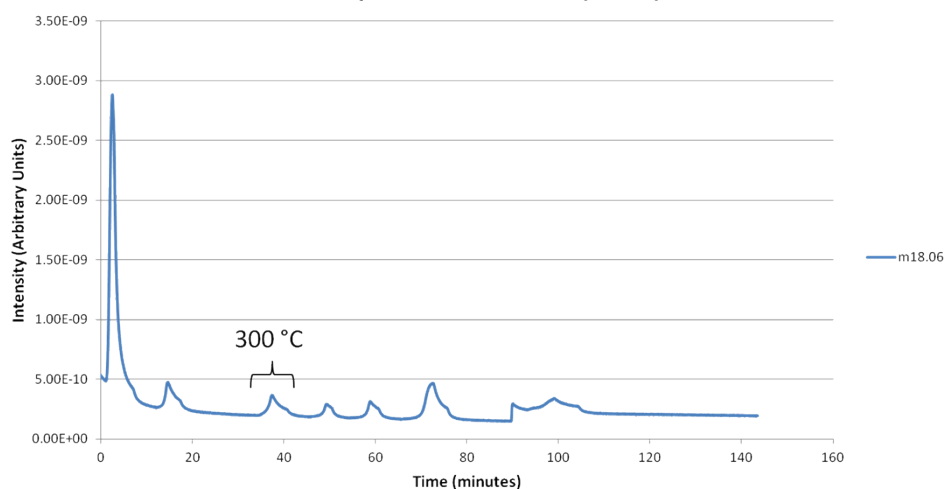
Mass spec information. The following masses were monitored: 2.31, 4.19, 18.06, 27.97, 31.94, 43.94, 64.96, 65.96, 76.98, 77.98, 78.98, 90.99, 91.99, 94, 105.01, 106.01, 108.01, 110.02, 123.03, 198.12, 199.12. Most of these fragments did not appear in the mass spec.



The following masses are shown above: 64.96, 65.96, 76.98, 77.98, 90.99, 91.99 (normalization factors = 8.5, 8.38, 5.2, 5.1, 5.04, 4.99, respectively), based on the expected fragments of aromatic molecules such as toluene and phenol.

Note: masses 91 and 92 are the major peaks associated with toluene. Toluene is the vast majority of products observed by mass spec with heating up to 400 °C and additional substantial products are observed only after the sample is heated to higher temperatures (e.g. 600 °C).

Mass Spectrum for m18.06 (water)

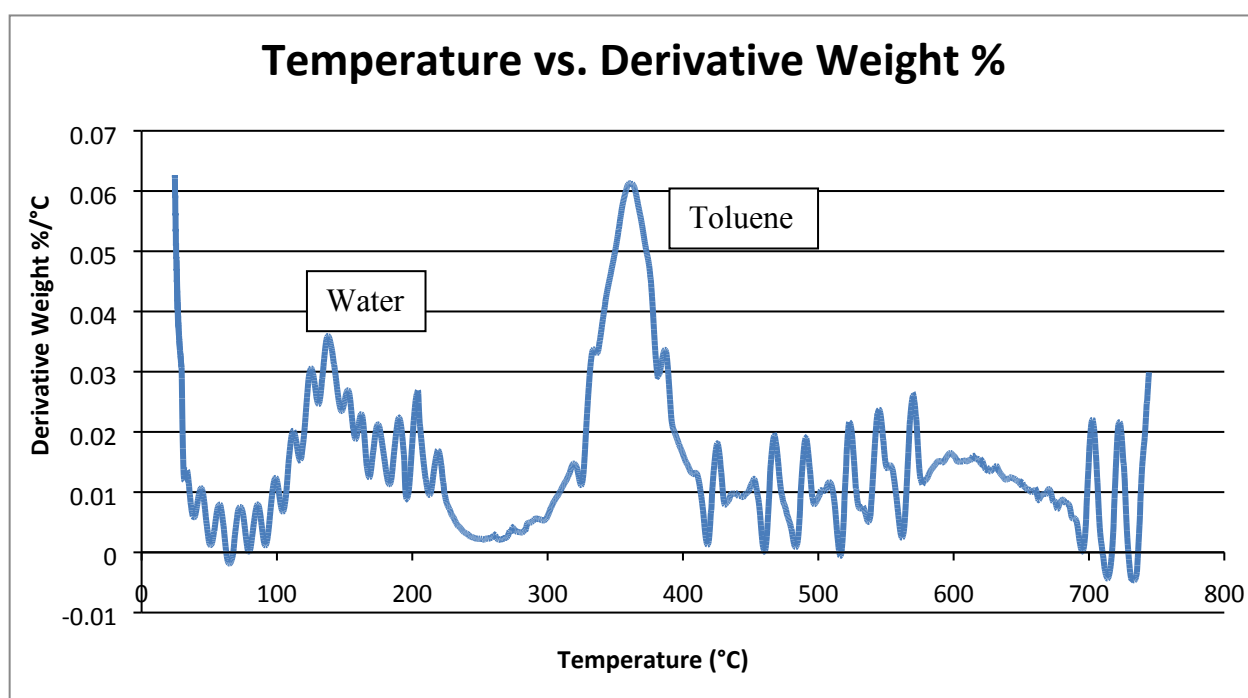
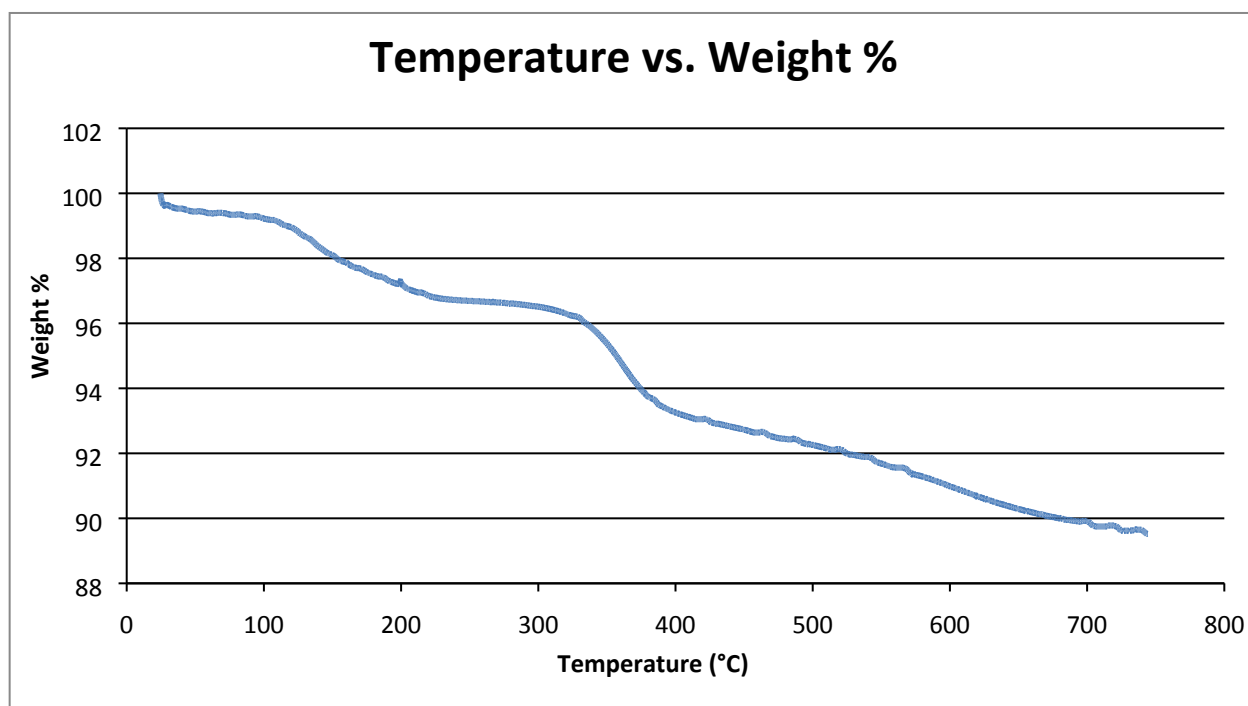


S4. Thermogravimetric analysis (TGA) data for BPEa-SBA-15

Below is the TGA data for BPEa-SBA-15 as conducted in a nitrogen atmosphere with a heating rate of 10° C per minute. The total weight loss by 600° C is ~9 wt %.

By dissolving the BPEa-SBA-15 silicate framework in 1 M NaOH followed by chemical analysis (see reference below), we obtain a molar density of 1.05 mmol of grafted BPEa per gram of BPEa-SBA-15. This indicates that the BPEa-SBA-15 is 21.0% BPEa by weight, and that 9.7% of the total weight of BPEa-SBA-15 is from the toluene moieties. The total weight loss during experiment is consistent with the following interpretation: essentially complete loss of the toluene moieties, without loss of the phenoxy moieties.

M. K. Kidder, P. F. Britt, Z. T. Zhang, S. Dai, E. W. Hagaman, A. L. Chaffee, A. C. Buchanan, *J Am Chem Soc* **2005**, *127*, 6353-6360.



S5. Peak area integrations and definitions of Si-OH: normalization of Si-OH band (~3745 cm⁻¹) to Si-O-Si framework band (~1000-1200 cm⁻¹) for determination of the number of freed silanols after heating.

Table S5a. Peak areas for Si-O-Si and Si-OH with different defined baselines and regions for comparison

	Baseline (cm ⁻¹)	Region (cm ⁻¹)	Peak Area (pure SBA-15)	Peak Area ((BPEa)-SBA-15)
Si-O-Si (case A)	1369 to 918	1369 to 918	2138	1806
Si-O-Si (case B)	1211 to 995	1207 to 998	243.9	209.15
Si-OH (case 1)	3750 to 3741	3750 to 3741	6.165	3.465
Si-OH (case 2)	3750 to 3723	3750 to 3723	25.689	16.536
Si-OH (case 3)	3758 to 3718	3756 to 3718	53.246	27.69

Table 2Sa shows the peak area ratios of the Si-OH band (~3745 cm⁻¹) and the Si-O-Si framework band (~1200-1000 cm⁻¹) of SBA-15. For the Si-O-Si stretches we picked two baselines for integration (case A and case B, we found that both these cases give the same result.). For the silanol stretches we used 3 different baselines for integration (referred to as case 1, 2, and 3) to get limits for the effects of baseline choice in that region.

Table S5b. Peak area normalizations of Si-OH to Si-O-Si

Case	Based on Si-O-Si (case A)		Based on Si-O-Si (case B)	
	Pure SBA-15	(BPEa)-SBA-15	Pure SBA-15	(BPEa)-SBA-15
Case 1	0.002883536	0.001918605	0.025276753	0.016567057
Case 2	0.012015435	0.009156146	0.105325953	0.079062874
Case 3	0.015332226	0.21831073	0.218310783	0.132393019

Table 2Sb shows values for the peak area normalization of Si-OH to Si-O-Si. As an example, the peak area normalization for the Si-OH (case 1) stretch to Si-O-Si (case B) in Pure SBA-15 was carried out using the relevant values in Table 2Sa: $6.165 / 243.9 = 0.025276753$

Table S5c. Peak area ratios of SiOH in (BPEa)-SBA-15 to SiOH in pure SBA-15.

	Case A Ratios	Case B Ratios
Case 1	0.665365246	0.65542664
Case 2	0.762032019	0.750649494
Case 3	0.615638715	0.606442877

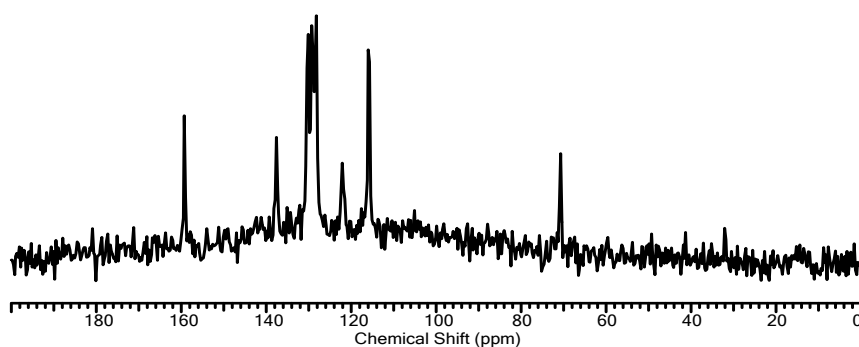
Table 2Sc shows the peak area ratios of SiOH of (BPEa)-SBA-15 to SiOH of pure SBA-15 based on cases A and B. Due to baseline considerations case 3 is the most accurate, and at least 40% SiOH groups became free after heating (BPEa)-SBA15 to 600 °C.

S6. ¹³C NMR Data

Solid state ¹³C NMR data of (BPEa)-SBA-15 show virtually no shift (<1 ppm) for the carbons in the toluene moiety relative to that of free BPE in solution or solid. We thus conclude that interaction occurs without any significant π -electron donation from the aromatic ring¹ of the toluene moiety (relative to some organometallic arene complexes²). Section S6.5 shows the NMR spectrum for the phenoxy moiety that remains in SBA-15 after BPEa-SBA-15 is heated.

1. Nelson, G. L.; Cargioli, J. D.; Levy, G. C. Solvent Effects in C-13 Nuclear Magnetic-Resonance - Electronic Perturbation of Aromatic Systems. *J Am Chem Soc* **1972**, *94*, 3089-&.
2. Ebsworth, E. A. V., D. W. H. Rankin, et al. (1991). *Structural Methods in Inorganic Chemistry*, CRC Press.

S6.1 BPE physisorbed on SBA-15 (solid state) (¹³C)

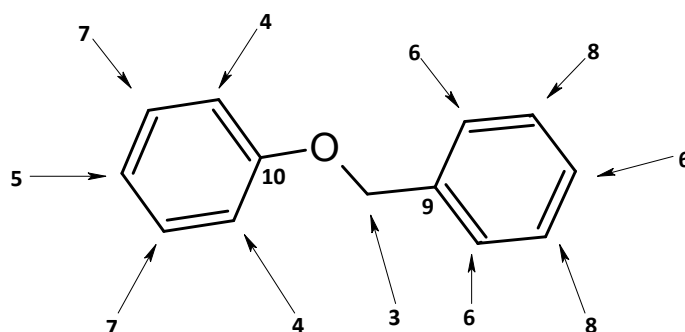


spectrumCP Table of peaks for the

No.	(ppm)	(Hz)	Height
1	32.13	5656.5	0.1118
2	37.68	6634.1	0.0059
3	70.71	12450.3	0.4241
4	115.96	20417.1	0.8578
5	122.06	21492.3	0.3847
6	128.17	22567.6	1.0000
7	129.28	22763.1	0.9598
8	130.11	22909.7	0.9233
9	137.61	24229.4	0.4918
10	159.26	28041.7	0.5816

¹³C spectrum of BPE physisorbed on the surface of SBA-15. Acquisition parameters were 3.25us 90 pulse and 75kHz decoupling with a 10 sec recycle delay with 512 transients. In the table of peaks 1&2 are side bands.

From Table of peaks for BPE Physisorbed



S6.2 BPEa-SBA-15 (solid state) (^{13}C)

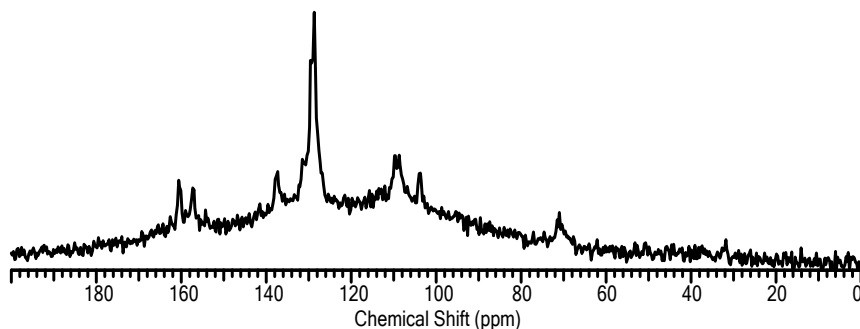
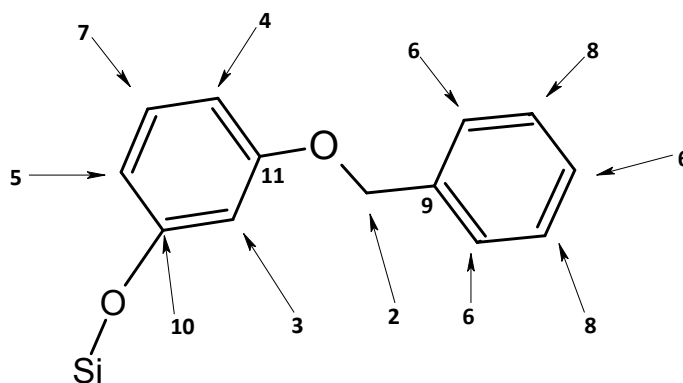


Table of peaks for the ^{13}C spectrum

No.	(ppm)	(Hz)	Height
1	31.85	5607.7	0.0264
2	70.99	12499.2	0.1429
3	103.74	18266.5	0.3119
4	108.74	19146.3	0.3887
5	109.57	19292.9	0.3872
6	128.73	22665.3	1.0000
7	129.56	22812.0	0.7937
8	131.50	23154.1	0.3709
9	137.33	24180.5	0.3186
10	157.32	27699.6	0.2477
11	160.65	28286.1	0.2810

^{13}C spectrum of BPEa-SBA-15. Acquisition parameters were 3.25us 90 pulse and 75kHz decoupling with a 20 sec recycle delay with 5120 transients. In table of peaks 1 is a sideband.

From Table of peaks for BPEa-SBA-15



S6.3 Pure BPE (solid state) (^{13}C)

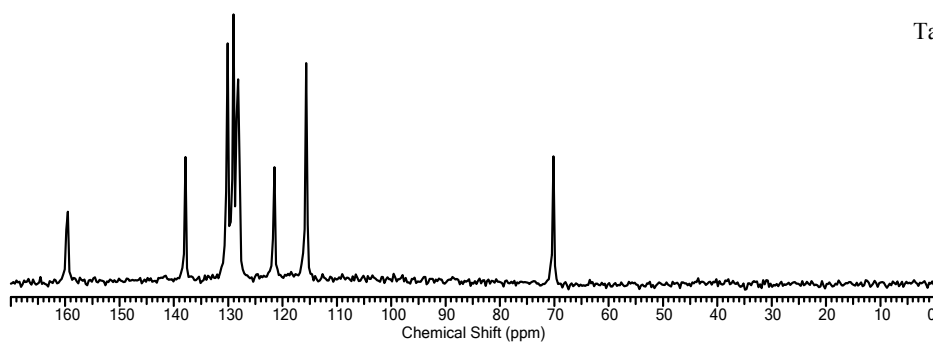
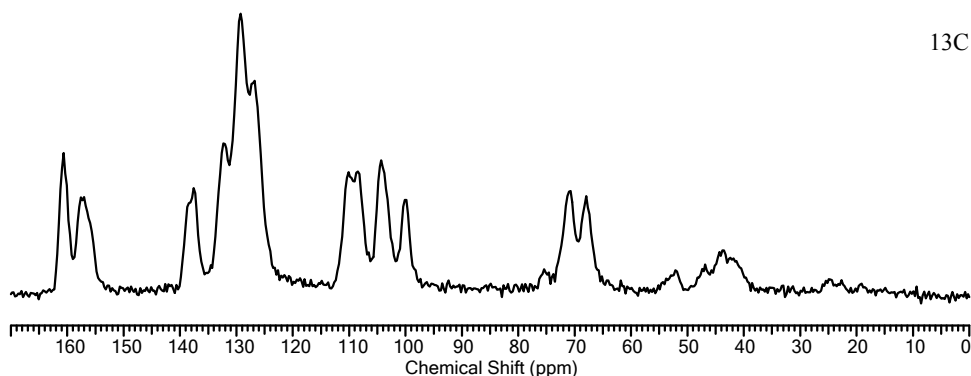


Table of peaks for the ^{13}C spectrum

No.	(ppm)
1	70.15
2	115.68
3	121.51
4	128.17
5	129.00
6	130.11
7	137.89
8	159.54

^{13}C spectrum of pure BPE. Acquisition parameters were 3.25us 90 pulse and 75kHz decoupling with a 10 sec recycle delay with 1024 transients at a MAS rate of 15kHz.

S6.4 Pure BPEa (¹³C CP)



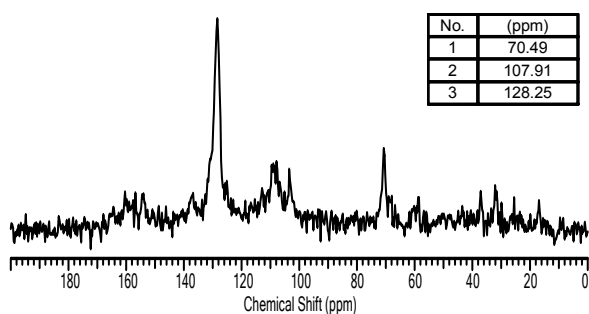
No.	(ppm)
1	67.93
2	70.71
3	99.86
4	104.30
5	108.46
6	110.13
7	126.78
8	129.28
9	132.33
10	137.61
11	157.59
12	160.65

¹³C CP spectrum of pure BPEa. Peaks at ~43ppm are spinning side bands and are not included in the table of peaks for CP spectrum.

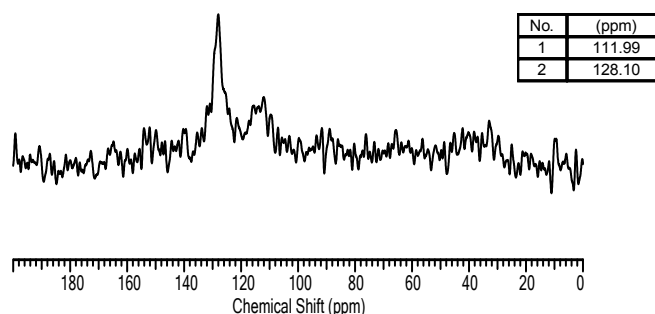
S6.5 BPEa-SBA-15 (¹³C CP) before and after heating

BPEa-SBA-15 sample ¹³C CP spectra.

Before heating:



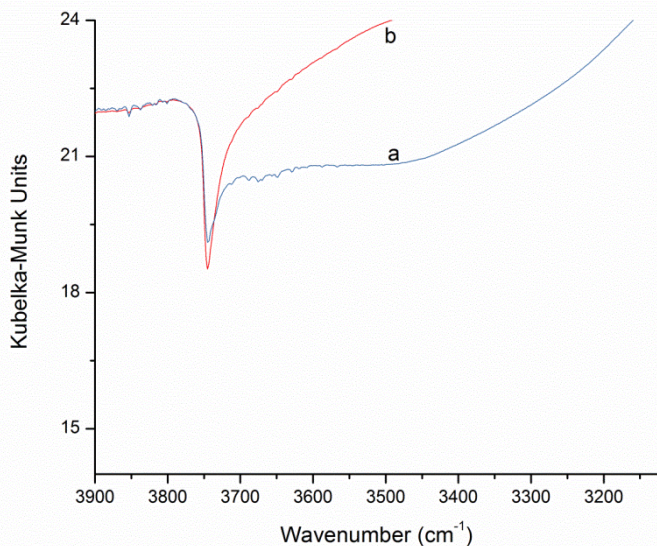
After heating:



¹³C CP spectra of BPEa-SBA-15 after heat treatment (200C for 1hr followed by 400C for 1hr) on the vacline. These spectra were acquired with a 10 sec recycle delay and 5120 scans. The above two spectra indicate that the BPEa-SBA-15 is intact prior to heating to 400 C, and that only the toluene moiety has left as indicated by the loss of the benzylic peak at ~70 ppm, with only a phenol type moiety remaining after heating to 400 C as indicated by the peaks at ~110 and ~128 ppm. This data is consistent with the DRIFTS and mass spec data.

S7. DRIFTS Spectra of Neat SBA-15 with and without adsorbed water

The below spectrum was obtained using the same experimental setup described in the main article, and the spectra correspond to neat SBA-15 (a) before heating and (b) after heating to 600 C. Spectrum (a) includes a broad hydroxyl band centered near $\sim 3450\text{ cm}^{-1}$ associated with adsorbed water.

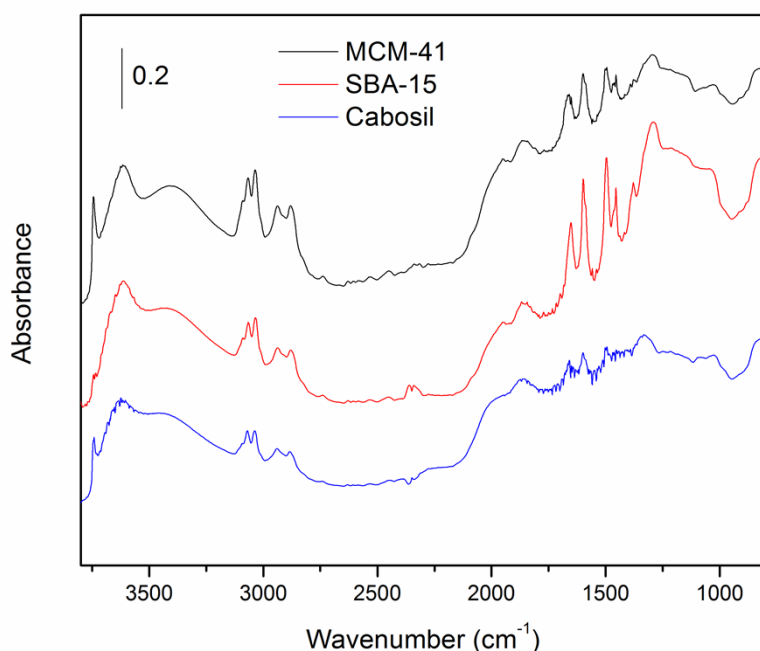


S8. NMR and IR data for physisorbed molecules

S8.1 IR data for BPE physisorbed on several silicate surfaces

Below we include drifts infrared spectra for BPE physisorbed on several silicate surfaces. Physisorbed BPE samples were prepared by solution deposition in benzene. The number of moles of BPE used was calculated to match the density of the tethered samples. Subsequently the benzene was allowed to evaporate prior to infrared measurements. It is assumed that all molecules from the solution remain adsorbed on the silicate surface, as a first approximation.

As can be seen, when BPE is physisorbed on these silicate surfaces, the infrared absorption in the CH stretching region has the same shape as the tethered BPE described in the main article, which has been interpreted in the main article as indicated of hydrogen bonding. It is not possible to perform in situ infrared temperature programmed decomposition of the physisorbed BPE, as the physisorbed BPE will desorb (and then pyrolyze) in the absence of tethering.

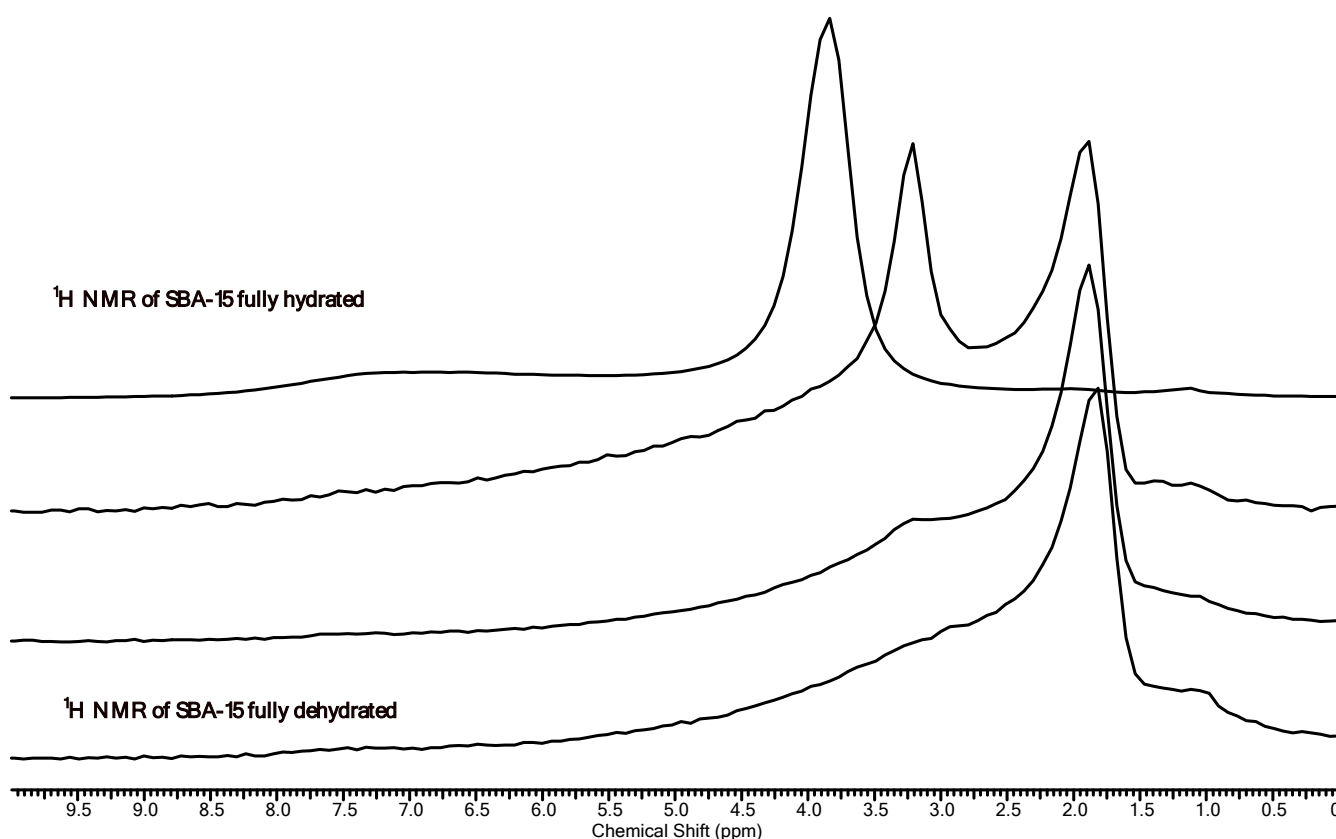


S8.2 NMR data for BPE physisorbed on SBA-15

Based on the ^{13}C NMR data BPE physisorbed on SBA-15 (section S6) we see essentially no shift for the carbons in the toluene moiety relative to that of free BPE in solution or solid. Thus, as noted in S6, the physisorption interaction occurs without significant π -electron donation from the toluene moiety. However, even with the physisorbed BPE there is evidence for hydrogen bonding between the toluene portion of the molecule and SBA-15 surface in the ^1H NMR data.

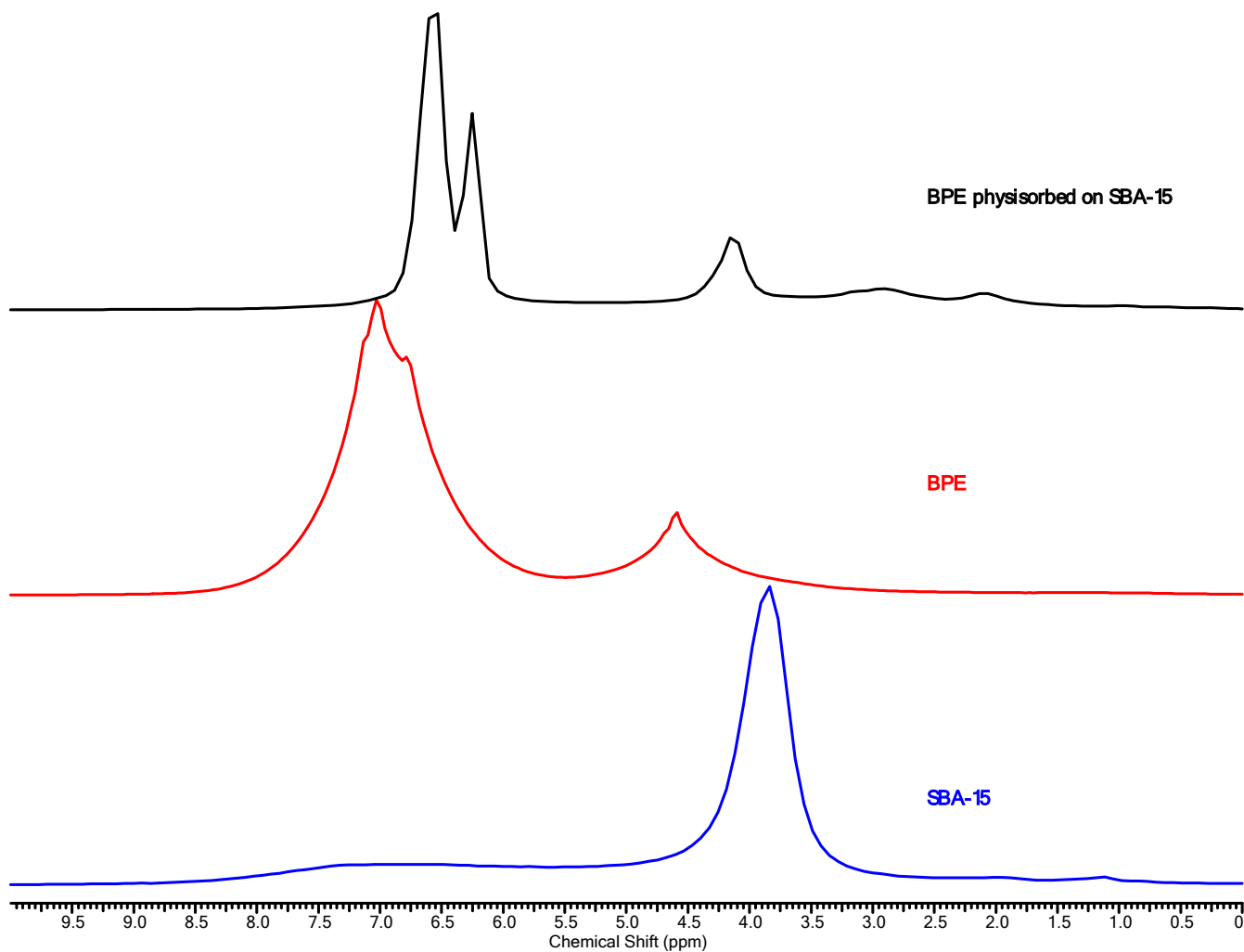
S8.2.1 ^1H NMR of SBA-15

^1H NMR of SBA-15 with varying amounts of H_2O



To assess where water peaks may appear in the spectrum we took ^1H NMR at various levels of hydration (arbitrary units) as shown in the stack plot of SBA-15 (from bottom to top) above. All spectra are normalized in this figure. As can be seen all peaks associated with water occur below ca. 4.5 ppm.

S8.2.2 ^1H ssNMR of SBA-15, BPE, BPE physisorbed on SBA-15



In the figure above of pure SBA-15 (blue), pure BPE (red), and BPE physisorbed on SBA-15 (black) it is clear that the peak at ca. 6.25ppm is indicative of a hydrogen bonding interaction. See e.g:

White, J. L.; Beck, L. W.; Haw, J. F. Characterization of Hydrogen Bonding in Zeolites by Proton Solid-State NMR Spectroscopy. *J Am Chem Soc* **1992**, *114*, 6182-6189.

S9. Discussion About Strength of Aromatic-Hydroxyl Bonding Complex

Pohle showed that the $\Delta\nu_{\text{OH}}$ shift of aromatic-hydroxyl interactions shows a functional form that is most consistent with a charge transfer model, and that the $\Delta\nu_{\text{OH}}$ shift can also be correlated with the Taft polar substituent constant for the aromatic ring (within series of electronically similar aromatic rings).^[1] The hydroxyl shifts observed due to the aromatic-hydroxyl coordination in BPEa-SBA-15 ($\nu_{\text{OH}}\approx 3475\text{ cm}^{-1}$ and $\Delta\nu_{\text{OH}}\approx 105$) are in excellent agreement with prior studies by Trombetta *et al.*^[2] of e.g. benzene and toluene on silica. We note that there are six types of hydrogen bonds,^[3] and similar OH shifts have been seen for a variety of adsorbates on a variety of surfaces,^[2, 4-5] and based on literature data a bigger shift is observed for more strongly acidic OH groups.^[6]

- [1] W. Pohle, *J Chem Soc Farad T 1* **1982**, 78, 2101-2109.
- [2] M. Trombetta, T. Armaroli, A. G. Alejandre, J. R. Solis, G. Busca, *Appl Catal a-Gen* **2000**, 192, 125-136.
- [3] P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Accounts Chem Res* **2009**, 42, 33-44.
- [4] A. Popov, E. Kondratieva, J. M. Goupil, L. Mariey, P. Bazin, J. P. Gilson, A. Travert, F. Mauge, *J Phys Chem C* **2010**, 114, 15661-15670.
- [5] K. Chakarova, K. Hadjiivanov, *Micropor Mesopor Mat* **2011**, 143, 180-188.
- [6] S. C. Ringwald, J. E. Pemberton, *Environ Sci Technol* **2000**, 34, 259-265.