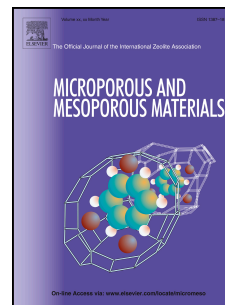


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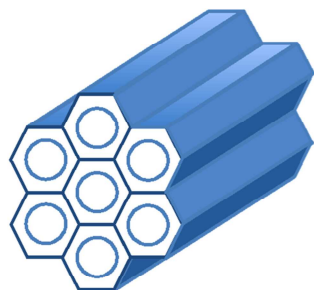
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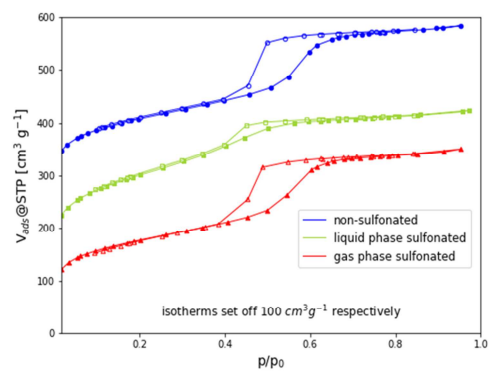


SBA-type mesoporous organosilica

Liquid phase sulfonation
Oleum 20, 100 °C, 24 h



Gas phase sulfonation
SO₃, ambient temp., 6 h



Ambient temperature gas phase sulfonation: A mild route towards acid functionalized ordered mesoporous organosilica

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Abstract

Sulfonation is a versatile method for the production of acidic materials, e. g. for applications in catalysis. In this study different sulfonation techniques for the production of acidic ordered mesoporous materials are investigated. SBA-15-like mesoporous organosilanes bearing aromatic moieties are sulfonated in the liquid phase with oleum as well as in the gas phase under significantly milder conditions with sulfur trioxide. Functionalization via liquid phase sulfonation at elevated temperatures proceeds at the expense of partial or complete collapse of the pore system. In contrast, gas phase sulfonation with sulfur trioxide at ambient temperature allows for similar sulfonation yields, while maintaining the textural properties due to the milder reaction conditions. Overall, acid functionalization of mesoporous organosilica using a gas phase sulfonation route is reported for the first time, enabling both high acid capacities and preservation of the pore structure.

Keywords

ordered mesoporous material; organosilica; SBA-15; gas phase sulfonation; acid functionalization

Acid catalysis plays a substantial role in the chemical industry. Owing to the large variety of chemical transformations that can be catalyzed by acids, research for the development of novel catalysts is still highly attractive.[1] Numerous recent studies aim at creating advanced solid acids as a replacement for liquid acids improving sustainability of industrial processes. Solid acids provide a lot of advantages over homogeneous acids - an easy separation strategy, prevention of waste and feasible catalyst recycling which entail ecologic and economic benefits. In the past decades, various solid acids have been developed with microporous zeolites and macroreticular ion exchange resins being the most prominent classes.[2] Previously, their high potential for acting as liquid acid replacement has been demonstrated in several studies.[3] However, both classes suffer from drawbacks hindering a broad use of those materials. Zeolites are limited to pore dimensions of a few nanometers restricting the applicable substrates, especially when the hydrodynamic radius of large substrates exceeds the pore size leading to inactive catalysts. Furthermore, zeolites can suffer from mass transport limitations based on the small pore sizes. On the other hand, macroreticular resins exhibit low specific surface areas and low (hydro)thermal stability.[4] Size selective catalysis due to the large pore system is not feasible for those materials. Various approaches have been taken to enhance catalytic performance by increasing pore sizes of zeolites as well as introducing mesopores post-synthetically.[5]

An alternative promising pathway is the development of mesoporous solid acids to combine the benefits of micropores and larger transport pores. Since the discovery of MCM-41 and SBA-15,[6] these types of ordered mesoporous silica have been extensively studied due to their high potential as defined and tailorable materials. Armengol et al. made use of the new materials by

integrating aluminium into an MCM-41 in analogy to zeolite synthesis.[7] The resulting materials were only weakly acidic and not as universally applicable as zeolites. A new concept of acid functionalization was introduced by Van Rhijn et al., who grafted mercaptopropyltrimethoxysilane (MPTMS) onto an MCM-41 surface followed by oxidation to a sulfonic acid.[8] Further advances in organosilane loadings were achieved by utilizing the co-condensation approach instead of grafting. Margolese et al. improved the incorporation of sulfonic acid sites drastically by co-condensating MPTMS with tetraethylorthosilicate (TEOS) in the SBA-15 synthesis under in-situ oxidation with H_2O_2 . [9] As the oxidation is quantitative in contrast to post-synthetic protocols, this approach leads to higher acid capacities, while also eliminating potentially problematic interference of left-over thiol groups. Further developments of mesoporous silica functionalization include the incorporation of aromatic moieties, which can either be sulfonated prior to or after the materials synthesis. Melero et al. used the sulfonated organosilane 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilan (CSPETMS) to incorporate acidic sites into SBA-15.[10] Lindlar et al. were the first to sulfonate an aromatic function post-synthetically with chlorosulfonic acid.[11] Further studies discussed a direct aromatic sulfonation of mesoporous organosilica.[12] In this context, periodic mesoporous organosilica (PMO) represent promising materials for sulfonation as they can bear a high organosilane content without the need to co-condensate TEOS.[13] Different groups have reported multi-step modification of ethylene-bridged PMO via alkylation [14] or epoxidation [15], respectively, followed by sulfonation as well as modification of aromatic PMO with chlorosulfonic acid. Although it is a universal method and requires only one modification step, the approach of a direct sulfonation of aromatic organosilica is reported in literature sparsely.[16] Particularly, basic knowledge about aromatic substitution reactions can be transferred onto these novel materials.

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In this work, we investigated the direct sulfonation of mesoporous organosilica materials containing three different types of incorporated organosilanes with varying molar ratios. Liquid phase sulfonation with oleum (20 wt.% SO₃) was applied and compared to a significantly milder sulfonation method based on gaseous sulfur trioxide. The efficiency of both methods was compared in terms of both sulfonation quality and structure preservation.

2.1 Chemicals

1,4-Bis(triethoxysilyl)benzene (96%), 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (95%), tetraethylorthosilicate ($\geq 99,0\%$) and P123 ($M_n \sim 5800$) were purchased from Sigma-Aldrich, phenyltriethoxysilane (98%) from Alfa Aesar. Oleum 20 (20% SO_3) was obtained from Honeywell. All chemicals were used without further purification.

2.2 Characterization

Elemental analysis was performed on a Vario EL from Elementar through sample oxidation at 925 °C, subsequent reduction at 650 °C and analysis of the gases with a TCD detector. Nitrogen physisorption was measured on a Quadrasorb SI instrument from Quantachrome Instruments following sample evacuation at 120 °C for 20 h. Specific surface areas (S_{BET}) were calculated from the BET-equation in a relative pressure (p/p_0) range of 0.05-0.3. Pore volume (V_p) and pore diameter (D_p) were determined using the NLDFT equilibrium model for nitrogen at -196 °C on silica with cylindrical pores. X-ray diffraction measurements were performed on a Siemens D5000 instrument at ambient temperature. Radiation wavelength ($\text{Cu-K}\alpha$) was 0.154 nm and measurement increments of 0.02° were recorded from 0.05° to 10°.

2.3 Co-condensation of organosilane into SBA-15-like materials

To a solution of P123, H_2O and HCl, the silica precursor TEOS was added at once under vigorous stirring and pre-hydrolyzed for 2 h before adding an organosilane of choice. The overall ratio was set to be organosilane:TEOS:P123:HCl: H_2O = $x:(1-x):0.017:1.22:126$ ($0 \leq x \leq 1$). The solution was stirred for 24 h at 35 °C and then altered without stirring at 100 °C

for 24 h. The product was filtered hot, washed with water and acetone and dried at 80 °C. Template removal was carried out by calcination in a muffle furnace in air at 380 °C for 12 h.

2.4 Liquid phase sulfonation

Organosilica (150 mg), oleum 20 (3 mL) and a magnetic stir bar were placed in a glass vial, sealed with a Teflon lined cap and heated to the desired temperature in a sand bath. The sulfonation was carried out under vigorous stirring for 24 h. After sulfonation, the cooled samples were carefully diluted with H₂O and washed thoroughly in the filter until the filtrate was pH neutral. The samples were dried in vacuo over molecular sieves at room temperature.

2.5 Gas phase sulfonation

Organosilica (300 mg) was placed in a gas phase reactor based on the setup by Richter et al.[17] Oleum 20 (10 mL) was present in the oleum reservoir vessel. For sulfonation, vacuum (below $5 \cdot 10^{-2}$ mbar) was applied to remove SO₃ as sulfonation agent from the liquid oleum into the gas phase and kept for 6 h at ambient temperature (23 °C). After sulfonation, the valve to the oleum reservoir was closed and vacuum was applied for 30 min to remove adsorbed species. The powder was washed thoroughly with water in the filter until the filtrate was pH neutral. The samples were dried in vacuo over molecular sieves at ambient temperature.

2.6 Ion exchange titration

Sulfonated organosilica (0.05 g) was suspended in a saturated solution of aqueous sodium chloride (10 g) and vigorously stirred for three days at ambient

temperature. The liquid containing exchanged protons from sulfonic acid groups was filtered using a Chromapore medium polar filter and diluted with H₂O. Dynamic titration with a solution of 0.01 M NaOH was carried out on the automatized titration device TitroLine alphaplus with a TA20plus adapter from SI Analytics.

Mesoporous organosilica were prepared in a co-condensation of an appropriate organosilane precursor and TEOS as the silica source according to the SBA-15 synthesis method as reported by the group of Ryoo.[18] Three different arene functionalities are shown in Figure 1. PTES participates in co-condensation via one silane linker, whereas bissilylated BTEB and BTBP are suitable for homogeneous incorporation following the PMO approach. Additionally, all organosilanes were used at varying molar ratios yielding a set of diverse materials. For each precursor, three samples were prepared with initial molar ratios of 10 mol%, 20 mol% and 30 mol%. Their properties are depicted in Table 1.

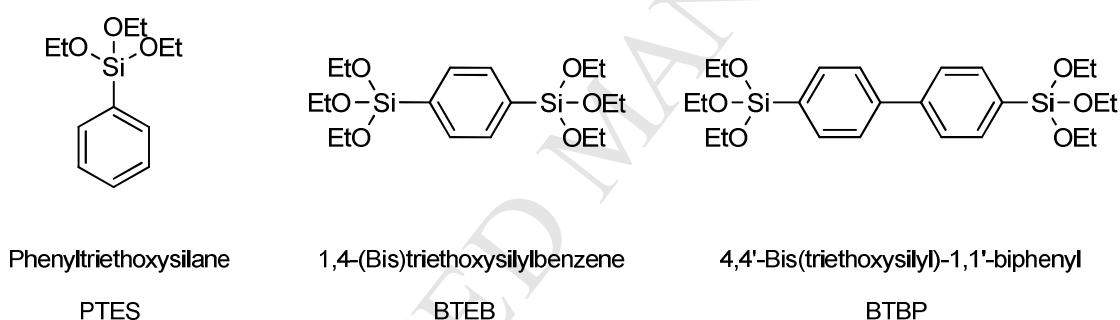


Figure 1. Organosilanes used for co-condensation in the synthesis of modified SBA-type materials.

All prepared samples exhibit high specific surface areas, micro- and mesoporosity, and pore diameters between 4.5-6.3 nm, all of which is characteristic of ordered SBA-type materials. As a general trend, lower pore volumes and diameters are obtained at increasing amounts of organosilane. Synthesis of PTES-modified materials with initial molar ratios of 10 mol% and 20 mol% yields powdery solids, whereas an increase to 30 mol% PTES only produces small amounts of wax-like material. This is indicative of strong

interaction between organosilane precursor and template, disrupting the process of self-organization to the point where ordered silane condensation is halted at a gel stage. Characterization of the samples with lower PTES content supports this presumption. According to elemental analysis, about 70 % of initial organosilane precursors could be incorporated into each material, confirming that indeed both TEOS and PTES participate in the self-organization process and subsequent silica condensation. The influence on structure formation can be observed from nitrogen physisorption isotherms presented in Figure 2 (for remaining isotherms of pristine materials, please see supporting information). In comparison to BTEB and BTBP, an initial molar ratio of 20 mol% PTES results in a notably wider and flatter hysteresis, indicating more unevenly distributed pore sizes and a significant loss of mesopore. Furthermore, the prominent (100) x-ray reflection of hexagonally structured materials decreases sharply at a higher molar ratio, thereby confirming the partial loss of order.

Although BTEB and PTES introduce the same organic functionality into the silica network, the bissilylated precursor is distributed more homogeneously and with less structural disruption due to its PMO suitability. Comonomer incorporation is virtually complete for an initial molar ratio of 10 mol% and is found to decrease only slightly at higher molar ratios. As observed in the physisorption isotherm, preservation of high order throughout the synthesis results in high specific surface areas and large pore volumes that decrease at higher molar ratios, thus matching the general trend. The (100) XRD reflection is clearly present in all BTEB-containing samples and indicates the ordered hexagonal structure in accordance with the isotherm shapes.

For the third comonomer to be incorporated, BTBP, the hydrodynamic radius is significantly larger than those of PTES and BTEB. Despite this, the synthesized materials exhibit properties broadly similar to BTEB-based samples. In comparison, elemental analysis gives somewhat lower degrees of

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incorporation for all initial molar ratios, which is attributed to the difficulties of accommodating larger biphenyl moieties inside the hexagonal lyotropic phase formed by the template molecules. Owing to the higher molar weight of BTBP, the resulting materials exhibit lower specific surface areas and pore volumes than their BTEB-containing pendants. According to XRD diffraction intensities, they are also slightly less ordered, but still remain well in the domain of periodically structured materials. Overall, synthesis of ordered SBA-type materials with varying degrees of organosilane incorporation was successful with the exception of samples prepared in the presence of high molar ratios of PTES.

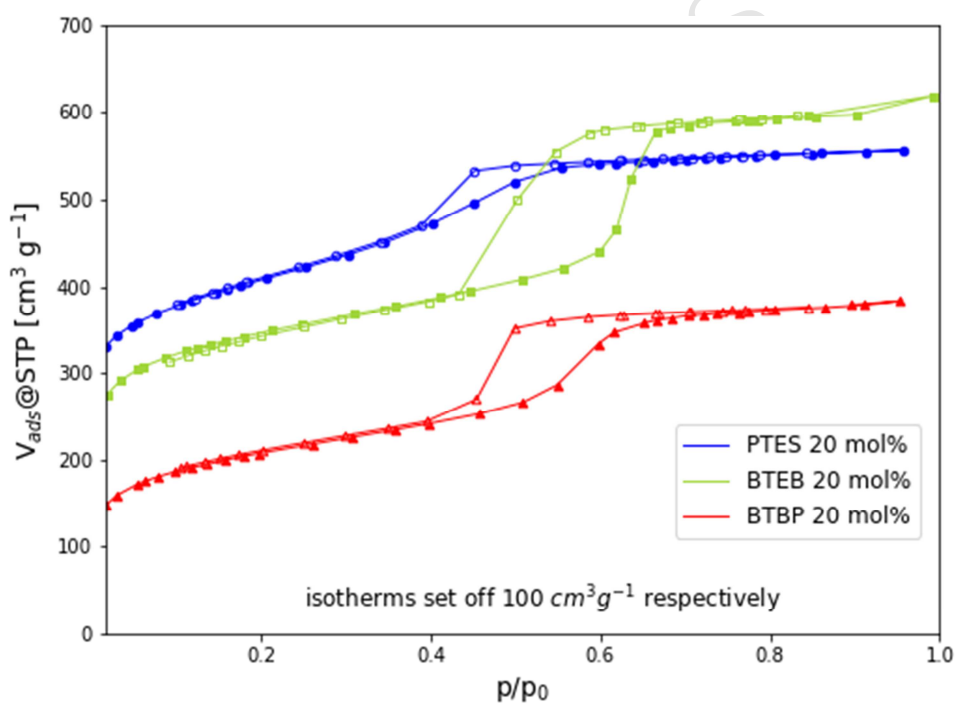


Figure 2. Nitrogen physisorption isotherms for three samples prepared with an initial molar ratio of 20 mol% of the respective organosilane.

The synthesized silica materials were sulfonated by an oleum treatment in the liquid phase as well as in gaseous phase by exposing the materials to sulfur trioxide, leading to solid materials with arene sulfonic acid groups. To judge the quality of a certain sulfonation method, the acid capacity obtained from ion

exchange titration and elemental analysis does not suffice. As an additional and more appropriate criterion, we propose the sulfonation yield, calculated from acid capacity and organosilane content, which states a percentage of sulfonated organic moieties in relation to the total amount of incorporated organic moieties ($n_{\text{SO}_3\text{H-aryl}}/n_{\text{aryl,total}}$). For a detailed description of sulfonation yield calculation, please see the supporting material.

Table 2 provides an overview of all sulfonated materials with resulting structural and acidic properties. Entries 1 to 8 correspond to liquid phase sulfonated samples. BTEB and BTBP afford similar sulfonation yields, which are significantly lower than in PTES-based materials. While the sulfonation yield does not follow a general trend at increasing molar ratios, higher organosilane content results in higher acid capacities. The highest achieved acid capacity of 1.21 mmol g^{-1} is well comparable to established sulfonation techniques (Entry 17). The lower performance of BTEB and BTBP in terms of sulfonation yields is not sufficiently explained due to the differences in electronic nature of the organosilanes, namely the number of deactivating, electron-withdrawing silicon oxide substituents attached to the organic moieties. Instead, the manner of incorporation seems to be of greater importance. Due to their bisilylated state, BTEB and BTBP can be introduced in great quantities and with high regularity. As a consequence, a certain amount of organic moieties is found inside the pore walls, where they are left inaccessible for reaction with sulfur trioxide. While PTES strongly interacts with structure formation and therefore produces materials of low order, organosilanes seem to be incorporated in locations of better accessibility, i.e. the pore surface, resulting in higher sulfonation yields.

Examining the structural properties of materials after completing liquid phase sulfonation, specific surface areas and pore volumes are found to decrease in general. Sulfonation accounts for this in two ways. Sulfonic acid groups attached to the pore surface decrease the pore size, thereby reducing pore volume and

surface available for adsorption while the accompanying weight gain further decreases the surface-to-mass ratio. The second aspect to be analyzed by nitrogen physisorption is the alteration of the structured (meso-)pore system during sulfonation, which is observed as changes in shape and position of the isotherm. In Figure 3, nitrogen physisorption isotherms of 12.1 mol% BTBP-containing material are shown before and after sulfonation. Hysteresis in the liquid phase sulfonated sample is shifted to lower relative pressures and steepness decreases sharply, indicating highly uneven pore sizes and almost complete loss of mesopore structure. This corresponds to a strongly disrupted pore system. While BTEB-based materials tend to be more resilient against structural degradation, loss of order can be observed for most samples incorporating PTES or BTBP. XRD measurements give additional evidence for this observation, as (100) diffraction intensities for those materials are notably lower compared to the non-sulfonated counterparts. In principal, lower initial order seems to ease structural breakdown throughout the liquid sulfonation process.

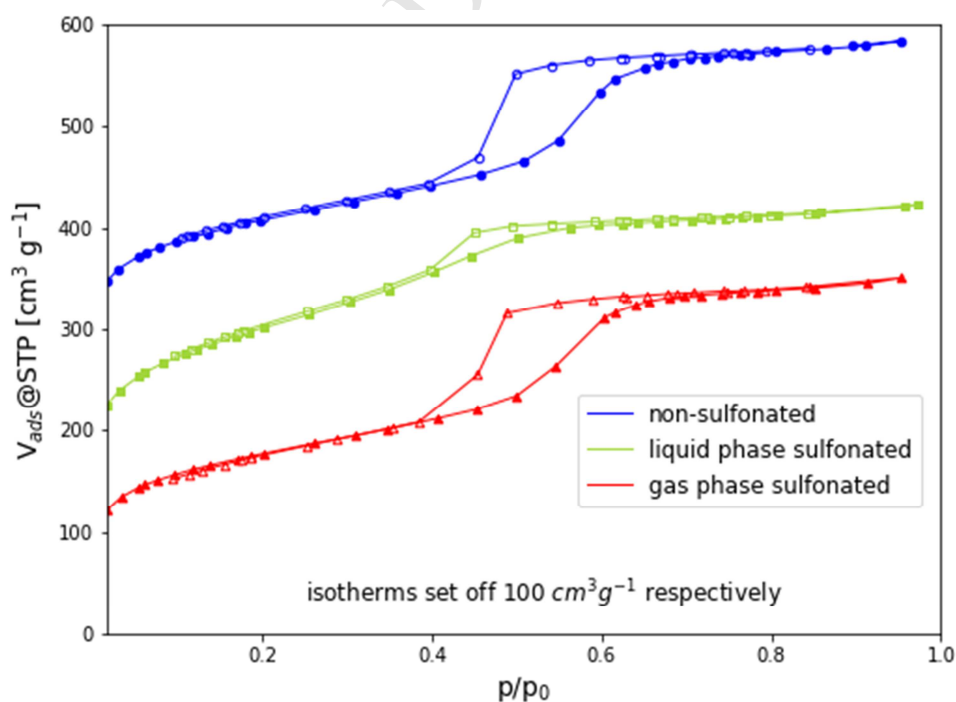


Figure 3. Isotherms of 12.1 mol% BTBP-containing samples before and after undergoing different sulfonation procedures.

Aiming to evade the structural degradation concomitant to liquid phase sulfonation, a possible milder gas phase reaction with sulfur trioxide at ambient temperature was investigated. Contrary to liquid phase sulfonation, where elevated temperatures promote diffusion and reaction rate, gas phase sulfonation benefits from lower temperatures due to improved adsorption. Entries 9 to 16 (Table 2) give the corresponding characterization data. Sulfonation yields and acid capacities obtained from gas phase sulfonation are higher on average than after liquid phase treatment. However, great variance is encountered as BTEB-derived samples exhibit both the lowest (0.19 mmol g^{-1} , entry 9) and highest acid capacity (1.72 mmol g^{-1} , entry 10), with the latter result being superior to most alternative sulfonation techniques (Entry 17). Replicating tendencies observed in liquid phase treatment, PTES proves easiest to sulfonate in gas phase reactions, whereas BTEB and BTBP achieve somewhat lower sulfonation yields. Taking into account the lower reaction temperature and shorter reaction time of only 6 hours, gas phase sulfonation proceeds with greater efficiency in terms of acidic properties.

In order to provide a superior sulfonation method, the gas phase reaction must also circumvent structural degradation, which proved to be the critical disadvantage in liquid phase treatment. Nitrogen physisorption data follows previous trends as specific surface area and pore volume decrease after gas phase sulfonation. This effect is even more pronounced compared to liquid phase treated samples. Exemplarily depicted in Figure 3 for 20 mol% BTBP-containing organosilica, the isotherm is only shifted to lower adsorbed volumes, while neither change in position nor deformation of the hysteresis occur. This indicates successful preservation of the uniformly structured pore system.

Whereas many, but not all materials undergo complete loss of textural properties during liquid phase sulfonation, not a single sample showed substantial distortion in uptake capacity or pore size distribution after gas phase treatment. Even PTES-containing organosilicas, which exhibit comparably low degrees of order in the pristine material, retain their pore structure notably better, as can be seen from (100) reflections in the XRD patterns presented in Figure 4. Therefore, gas phase treatment constitutes a significantly milder method compared to liquid phase sulfonation, especially when considering arene functionalization in organosilica materials of lower initial order.

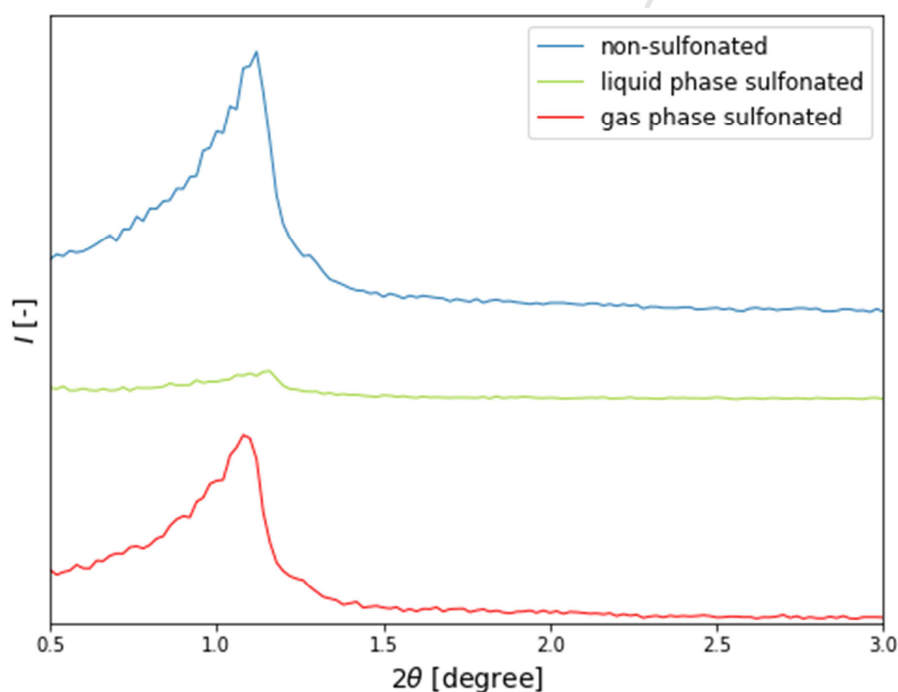


Figure 4. X-ray diffraction patterns at small angles for samples containing 10 mol% PTES, before and after undergoing different sulfonation procedures.

In summary, we applied liquid and gas phase sulfonation in the acid functionalization of organosilane-modified SBA-type materials. Liquid sulfonation conducted at elevated temperatures resulted in partial or complete disruption of the pore structure. Hence, the advantages of high specific surface areas and defined pore size distributions are lost. The alternative gas phase sulfonation at ambient temperature enables comparable sulfonation yields within much shorter reaction time, thereby proceeding with greater efficiency. At the same time, no structural degradation was observed in any samples. Less resilient materials in particular maintained their uniformly structured pore system far better. Overall, it constitutes an effective and mild method of sulfonation for any organic or organic/inorganic hybrid material bearing arene functionalities. Thus, it opens up versatile possibilities for acid functionalization under mild conditions.

5. Acknowledgements

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7. Tables

Table 1.

Organosilane	Molar ratio applied [mol %]	Molar ratio incorporated [mol %]	$S_{\text{BET}}^{\text{b}}$ [m ² g ⁻¹]	V_{p} [cm ³ g ⁻¹]	D_{p} [nm]	2θ [°]	$d(100)$ [nm]	Intensity [-]
PTES	10	7.2	782	0.779	5.7	1.12	7.9	2639
	20	13.7	748	0.551	4.5	1.12	7.9	970
	30	no	product	-	-	-	-	-
BTEB	10	10.6 ^c	1161	1.169	6.3	0.92	9.6	3718
	20	18.5	864	0.803	5.1	0.96	9.2	2831
	30	22.7	751	0.643	5.2	0.96	9.2	4659
BTBP	10	6.4	816	0.710	5.2	1.00	8.8	2373
	20	12.1	732	0.593	5.2	0.96	9.2	2041
	30	18.2	579	0.512	5.1	0.94	9.4	3585

^a determined by carbon elemental analysis; ^b calculated at $p/p_0 = 0.05-0.3$; ^c Incorporated molar ratio exceeding applied molar ratio is attributed to fluctuations of incorporation throughout the material.

Table 2.

Entry	Organosilane	Molar ratio incorporated	S _{BET}	V _p	Intensity	Acid capacity	Degree of incorporation	Sulfonation yield
		[mol%]	[m ² g ⁻¹]	[cm ³ g ⁻¹]	[-]	[mmol g ⁻¹]	[%]	[%]
1 ^a	BTEB	10.6	780	0.816	1126	0.44	106	32
2 ^a		18.5	716	0.673	2819	0.61	92	30
3 ^a		22.7	565	0.443	1318	1.19	76	52
4 ^a	BTBP	6.4	752	0.632	333	0.36	63	43
5 ^a		12.1	724	0.499	177	0.40	61	30
6 ^a		18.2	773	0.540	99	0.65	61	37
7 ^a	PTES	7.2	716	0.719	286	0.77	72	71
8 ^a		13.7	573	0.445	109	1.21	68	64
9 ^b	BTEB	10.6	781	0.761	1306	0.19	106	14
10 ^b		18.5	701	0.630	4514	1.72	92	85
11 ^b		22.7	525	0.516	3042	0.95	76	41
12 ^b	BTBP	6.4	723	0.674	571	0.23	63	27
13 ^b		12.1	625	0.543	401	0.76	61	56

14 ^b		18.2	388	0.351	1933	0.92	61	53
15 ^b	PTES	7.2	716	0.746	1862	0.48	72	44
16 ^b		13.7	573	0.459	688	1.40	68	75
17 ^c	Melero et al.					1.39		

^aLiquid phase sulfonated for 24 h at 100 °C; ^bGas phase sulfonated for 6 h at ambient temperature; ^c Alternative preparation method for reference[10].

Figure 1. Organosilanes used for co-condensation in the synthesis of modified SBA-type materials.

Figure 2. Nitrogen physisorption isotherms for three samples prepared with an initial molar ratio of 20 mol% of the respective organosilane.

Figure 3. Isotherms of 12.1 mol% BTBP-containing samples before and after undergoing different sulfonation procedures.

Figure 4. X-ray diffraction patterns at small angles for samples containing 10 mol% PTES, before and after undergoing different sulfonation procedures.

9. Figures

Figure 1:

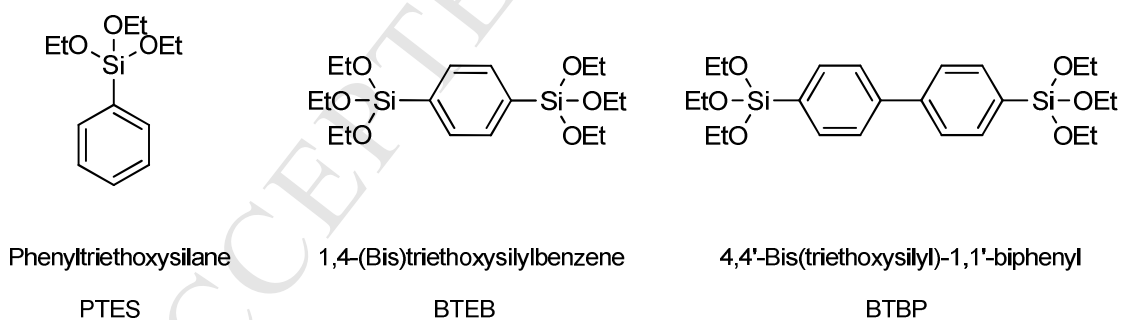


Figure 2:

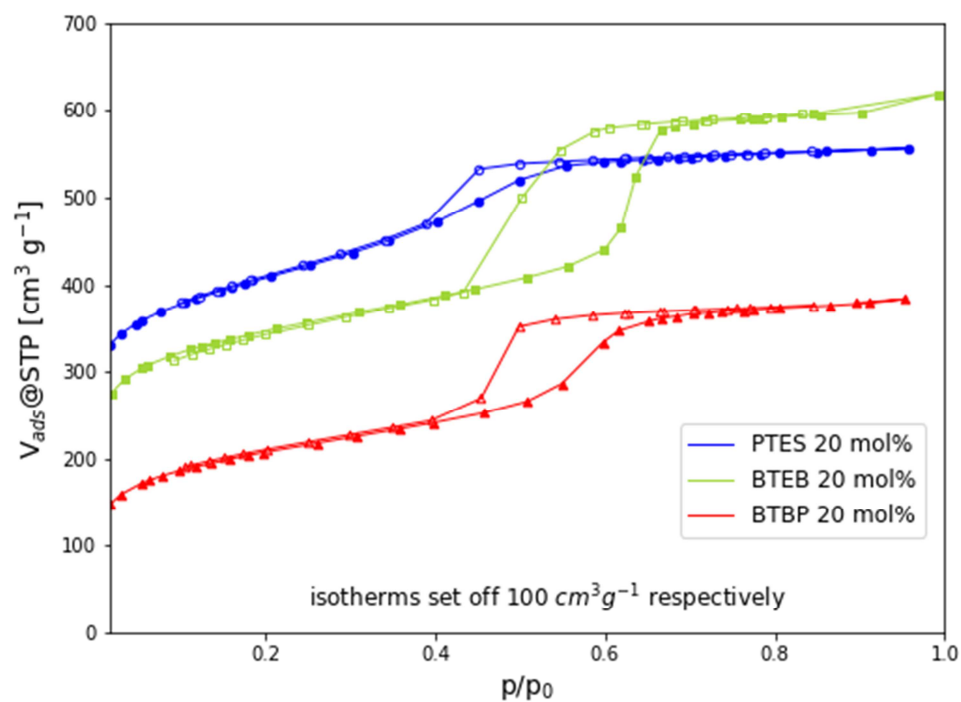
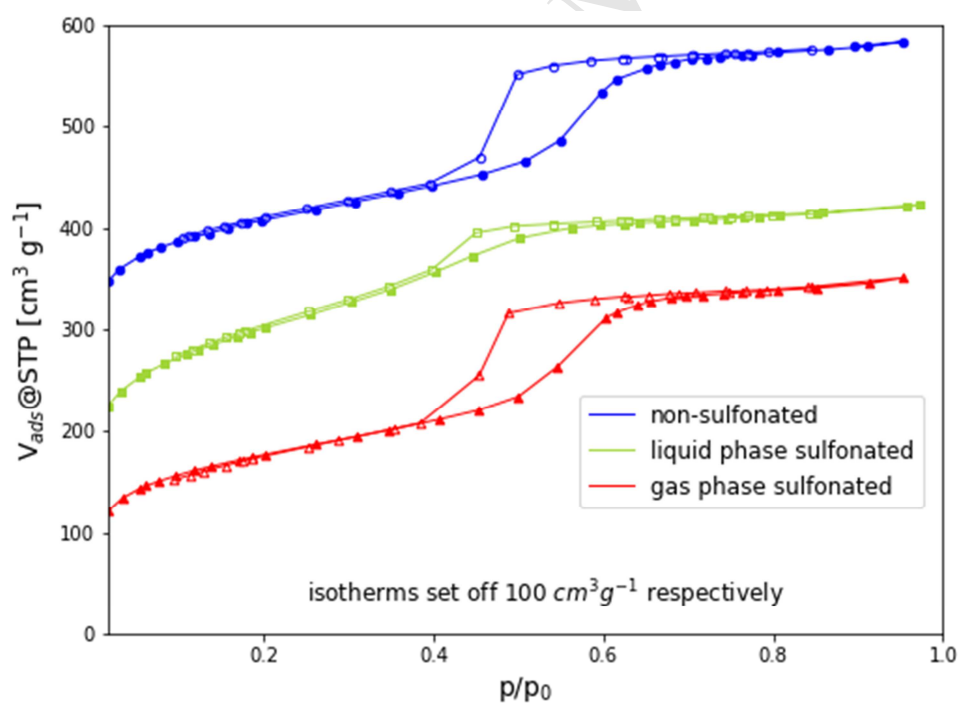
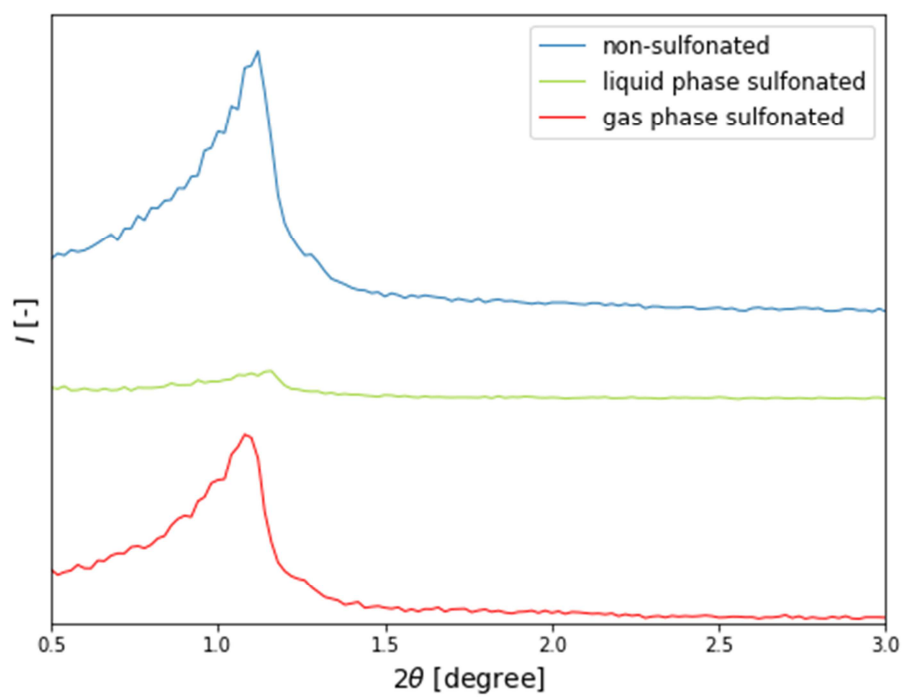


Figure 3:





- Mesoporous SBA-type organosilica have been synthesized using the PMO approach
- Acid functionalization was carried out via liquid phase and gas phase sulfonation
- Liquid phase sulfonation facilitated pore structure breakdown
- A new gas phase technique enables mild and efficient functionalization that maintain textural and structural properties