

# ADSORPTION OF BTEX VAPOURS USING MODIFIED SILICA AEROGELS OF DIFFERENT HYDROPHOBICITY

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Silica monolith aerogels with different degrees of hydrophobicity by incorporating methyltrimethoxysilane (MTMS) or trimethylethoxysilane (TMES) in standard sol-gel synthesis were prepared. Excellent properties of aerogels, obtained with the sol-gel synthesis, were preserved with supercritical drying with CO<sub>2</sub>. The degree of hydrophobicity of the aerogels was tested by measuring the contact angle ( $\theta$ ) of a water droplet with the aerogel surface. The organic and inorganic bonds forming the aerogel structure were studied by Fourier transform infrared spectra (FTIR). From the measurements with Differential scanning calorimeter (DSC) thermal stability of the aerogels, in terms of retention of hydrophobicity, was observed. The pore texture and BET surface areas of some samples were determined by nitrogen physisorption. The adsorption capacity measurements of different silica aerogels were done by mini-column method. Continuous adsorption measurements show that silica aerogels are excellent adsorbents of benzene, toluene, ethylbenzene and xylene (BTEX) vapours from waste gas stream. The possibility to tailor hydrophobicity and consequently moisture resistance of silica aerogel adsorbents and their repeated use in many adsorption/desorption cycles make them superior to conventional adsorbents as silica gel and activated carbon.

**Key words:** silica aerogel; hydrophobicity; vapour phase adsorption; BTEX removal; porosimetry.

## INTRODUCTION

Silica aerogels are extremely porous (up to 99%) nanostructured materials with high specific surface areas (500-1000 m<sup>2</sup>g<sup>-1</sup>) and low density (as low as 5 kgm<sup>-3</sup>). These features lead to unique properties, such as small index of refraction (1.008 to 1.4), low elastic modulus (<0.5 MPa), low thermal conductivity (0.01 Wm<sup>-1</sup>K<sup>-1</sup>) and to excellent accessibility of the inner surface through open porous network. One of the most important properties of silica aerogel is also the possibility to control its hydrophobicity.

The production of hydrophobic silica aerogels has become an important and intensive area of research, as for many of the scientific and technological applications of the aerogels, aerogels with different degrees of hydrophobicity are needed. Aerogels, based on tetramethoxysilane (TMOS) precursor, are hydrophilic and become wet with atmospheric moisture or water, but with appropriate chemical modification, the surface of the aerogel can be rendered hydrophobic so that the water molecules will be repelled [1-5]. The principal reason for hydrophilicity of silica aerogels is the presence of Si-OH groups in aerogel structure as they promote the adsorption of water. By replacing Si-OH groups with hydrolytic stable Si-R

groups ( $R = \text{CH}_3$ ), hydrophobic silica aerogels are obtained, because the adsorption of water is hindered.

Due to these remarkable properties, aerogels could, besides other well-known applications [6], serve as good adsorbents for water and other organic vapours [7-9]. We have prepared silica monolith aerogels with different degrees of hydrophobicity by incorporating methyltrimethoxysilane (MTMS) or trimethylethoxysilane (TMES) in standard sol-gel synthesis. The aim of the study was to determine the feasibility of using these materials in adsorption process of BTEX vapours from waste gas streams and to provide adsorption capacity data to compare with AC and silica gel. Rapid small-scale mini-column tests were carried out to simulate dynamic adsorption of BTEX vapours and to study the performance of six different silica aerogels and two commercial adsorbents.

Benzene, toluene, ethylbenzene, and xylene (BTEX) are some of the most common air pollutants that need to be controlled according to increasingly stringent environmental regulations. Atmospheric emissions of these volatile organic compounds from industrial facilities and motor vehicle exhaust cause serious environmental problems and financial losses. They are toxic and carcinogenic to human health. The most commonly used process of separation is adsorption for which adsorbents with high specific surface areas and possibility to be used in many cycles are needed. Small pores, such as micropores and mesopores, result in large specific surface area responsible for adsorption. Pore size, pore distribution and surface area, as well as pore surface chemistry, are the major factors in the adsorption process [10-12]. Silica aerogels meet these conditions because these materials have high specific surface areas, they are stable even after many adsorption/desorption cycles with no loss of efficiency, they are easy recovered and they exhibit capacities which enormously exceed that of commonly used adsorbents.

## MATERIALS AND METHODS

### Aerogel Preparation

Silica aerogels of different degree of hydrophobicity were prepared by sol-gel processing of a tetramethoxysilane (TMOS - Aldrich, 98%) with methyl groups containing alkoxides: methyltrimethoxysilane (MTMS - Aldrich, 98%) and trimethylethoxysilane (TMES – Fluka, 97%). For synthesis of silica aerogels also methanol (Merck, p.a.), 25 wt.% solution of  $\text{NH}_3$  (TKI Hrastnik, p.a.) and distilled water were used.

Silica gels that have beside hydroxyl groups also methyl groups were synthesised by mixing TMOS, MTMS or TMES, methanol, water and ammonium hydroxide in different molar ratios as described in our previous article [9] Experimental data are given in table 1. The apparatus used for sol-gel synthesis is already presented in previous articles [13].

**Table 1:** Experimental data for the preparation of different silica aerogels.

Sample	Molar ratio		Precursors [mol]				Gel time [min]
	MTMS or TMES/TMOS	MTMS or TMES	TMOS	MeOH	H <sub>2</sub> O	NH <sub>4</sub> OH	
TMOS1	0	0	1	6	5	0.005	9
MTMS1	2	0.667	0.333	4.333	3.333	0.115	66-71
MTMS2	5	0.833	0.167	3.917	3.167	0.143	66-74
MTMS3	10	0.909	0.091	3.727	3.091	0.155	58-84
MTMS4	$\infty$	1	0	3.5	3	0.17	50-75
TMES1	5	0.833	0.167	6	1.5	0.005	< 16h

The second step in the production of aerogels was the drying of wet gels with supercritical carbon dioxide at 40 °C and 100 bars [13]. For further use as adsorbent of BTEX vapours from air aerogels were ground to appropriate size and filled in mini-column.

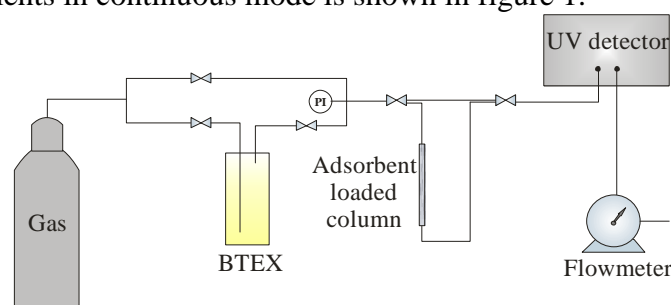
### Aerogel Characterization

The hydrophobicity of aerogels was determined by measuring the contact angle ( $\theta$ ) of a sessile drop of water on the surface of a monolithic aerogel. For each measurement, a photograph of the droplet was taken and contact angle was measured directly from the photographic image. The method is described in details in our previous article [9].

The organic and inorganic bonds forming the aerogel structure were studied by Fourier transform infrared spectra (FTIR). From the measurements with Differential scanning calorimeter (DSC) thermal stability of the aerogels, in terms of retention of hydrophobicity, was observed. The pore texture and BET surface areas of some samples were determined by nitrogen physisorption using a TriStar 3000 surface area and porosimetry analyser from Micromeritics.

### Adsorption Measurements

Silica aerogels of different degrees of hydrophobicity were used for the adsorption of BTEX vapours from gas stream saturated with one of the compounds separately at ambient temperature. Aerogels were ground into small pieces (size less than 0.25 mm) using mortar and pestle. Adsorbent loaded mini-column (100×4.6 mm) was first dried at 100 °C to remove the adsorbed moisture. Then the air saturated with organic compound at room temperature was passed through the column. For monitoring adsorption process of BTEX vapours from air UV spectroscopy was used. The column with adsorbent was weighed before and after adsorption process and the adsorption capacities of aerogels were determined gravimetrically. For determining reusability, the adsorbed BTEX was stripped from the column with hot inert gas and the adsorbent was reused in next cycles. The adsorption capacities of silica gel (MP SILICA, particle size 100-200  $\mu\text{m}$ , specific surface area 500-600  $\text{m}^2/\text{g}$ ) and activated carbon (Bayer 01E 1179, particle size 150-250  $\mu\text{m}$ , specific surface area  $\sim 500 \text{ m}^2/\text{g}$ ) were also determined for the comparison with aerogels. The flow sheet of apparatus used for adsorption capacities measurements in continuous mode is shown in figure 1.



**Figure 1:** Flow sheet of apparatus for continuous adsorption process.

## RESULTS

### Characterization of Aerogels

For adsorption process of BTEX vapours from air silica aerogels with different degree of hydrophobicity were prepared by varying molar ratios MTMS/TMOS or TMES/TMOS. Its effect on hydrophobicity was already studied in our previous article [9]. Hydrophobicity of aerogel adsorbents was tested and contact angles that were measured directly from the

photograph image (except for aerogel sample TMES1) are given in table 2. For the aerogel TMES1, it was impossible to obtain a contact angle as the water droplet deposited on the surface was repulsed immediately, leaving a completely dry surface. Because of that it was decided to attribute a contact angle of  $\sim 180^\circ$  to this aerogel.

**Table 2:** Properties of different modified silica aerogels.

Sample	Molar ratio MTMS or TMES/TMOS	Contact angle $\theta$ [°]	BET surface area [m <sup>2</sup> /g] <sup>1</sup>	Pore volume [cm <sup>3</sup> /g]	Average pore size [nm]	C value
TMOS1	0	/	812	3.67	18.1	90.0
MTMS1	2	133	719	2.28	12.7	47.6
MTMS2	5	144	560	1.26	9.0	99.4
MTMS3	10	157	112	0.13	5.8	5.9
MTMS4	$\infty$	173	3.65 <sup>2</sup>	0.005	4.8	-457
TMES1	5	$\sim 180$ <sup>3</sup>	732	2.79	15.3	32.0

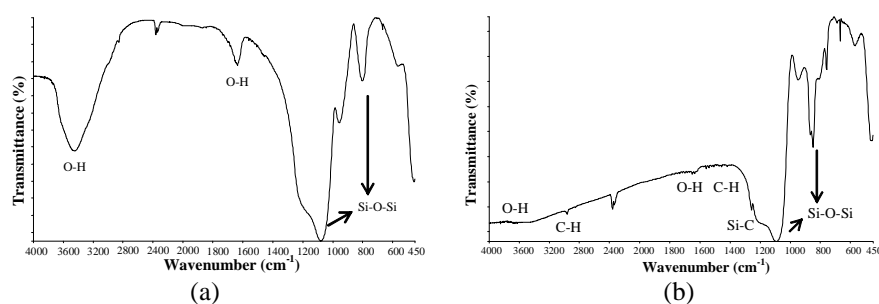
<sup>1</sup> Determined using Braunauer-Emmett-Teller (BET) method using N<sub>2</sub> gas adsorption.

<sup>2</sup> Nitrogen sorption is not appropriate method, because of highly microporous material.

<sup>3</sup> Water droplet deposited on the surface was repulsed immediately, leaving a completely dry surface.

The results of the specific surface area, total pore volume and pore diameter measurements (table 2) show that with the incorporation of MTMS or TMES the specific surfaces are lowered. By increasing the amount of added MTMS, specific surface area, pore volume and average pore size decrease, because co-hydrolysis of MTMS and TMOS proceeds one after another and thus results in different microstructures [1, 9]. From table 2 it can also be observed that with TMES modification compared to MTMS modification higher degree of hydrophobicity can be achieved at lower molar ratios and properties such as specific surface and pore volume are not significantly changed.

In figure 2 the FTIR investigations of the unmodified hydrophilic silica aerogel (TMOS1) and with TMES modified hydrophobic silica aerogel (TMES1) are shown. The peaks at around 1100, 800 and 470 cm<sup>-1</sup> are due to asymmetric, symmetric and the bending modes of SiO<sub>2</sub> respectively. The FTIR spectrum of aerogel TMOS1 shows major peaks also at around 3500 and 1650 cm<sup>-1</sup>, which are the evidence of O-H bonding. The residual Si-OH groups are the main reason of hydrophilicity of the aerogels. On FTIR spectrum of aerogel TMES1 peaks around 2900 and 1450 cm<sup>-1</sup>, which are due to C-H bonds and a peak around 1250 cm<sup>-1</sup>, which is related to Si-C bonds, are also observed. Only small peaks at around 3500 and 1650 cm<sup>-1</sup> are the evidence of O-H bonding. This is a proof of hydrophobic nature of TMES1 aerogel. FTIR spectrum of MTMS modified aerogel is given in our previous article [9].



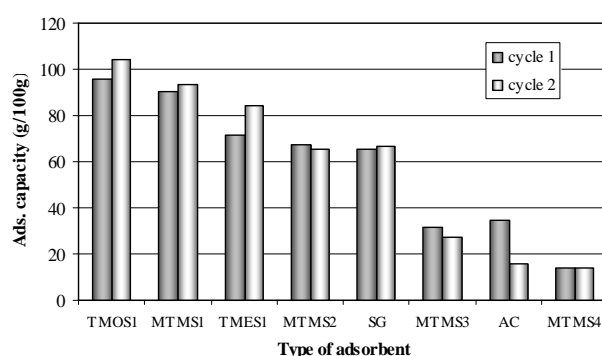
**Figure 2:** FTIR absorption spectra: (a) unmodified silica aerogel (TMOS1) and (b) with TMES modified silica aerogel (TMES1).

From DSC and TG measurements for aerogel sample TMES1 and MTMS4 it was observed that there is a very little weight loss up to a temperature of 300 °C and the further increase of temperature causes weight loss along with exothermic peak corresponding to the oxidation of surface organic (CH<sub>3</sub>) groups. Because of this, aerogel samples become hydrophilic after heating above a temperature of around 300 °C.

### Adsorption capacity measurements

Adsorbents were packed in mini-column through which the flow of air saturated with toluene, benzene, ethylbenzene or xylene was passed. The flow through the column was kept between 5-10 L/h. At the outlet, effluent concentration was monitored with UV detector and by this it was possible to follow the process of adsorption. The adsorption capacity was determined gravimetrically and calculated from mass difference of column before and after the adsorption process.

The adsorption capacities of benzene vapours of all six aerogels and two commercial adsorbents tested in two repeated cycles are presented in figure 3. From the results it can be seen that there is no difference in adsorption capacity in both cycles for aerogel adsorbents and silica gel. For active carbon a big drop in adsorption capacity in the second cycle is observed. The results also show that the adsorbent with the highest adsorption capacity of benzene vapours from air is hydrophilic silica aerogel, and its adsorption capacity exceeds that of AC or SG significantly. With the incorporation of MTMS in sol-gel synthesis and consequently by increasing a degree of hydrophobicity, the performance of aerogels in sense of adsorption of benzene vapours is lowered. Contrary to MTMS based aerogels, for TMES based silica aerogel which is also superhydrophobic, higher specific surface area is determined and consequently also higher adsorption capacity of benzene vapour. Because of its hydrophobicity it does not remove water vapour from waste gas streams but only BTEX vapours. Water vapour is ubiquitous in indoor environments and in many types of industrial gas streams and it can competitively adsorb onto adsorbent or even alter the adsorption capacity [14]. From this point of view, the hydrophobic aerogel (TMES1) is superior adsorbent of BTEX vapours compared to other used adsorbents, especially to two commercial ones (SG and AC).



**Figure 3:** Comparison of adsorption capacities of different adsorbents used for the removal of benzene from air in two repeated adsorption/desorption cycles.

The comparison between two aerogel adsorbents (TMOS1 and TMES1) and two commercial adsorbents (SG and AC) used as adsorbents of BTEX vapours is given in table 3. The amounts adsorbed on adsorbents are almost the same irrespective of adsorbate (each of BTEX compound). The highest adsorption capacity has aerogel TMOS1 followed by aerogel TMES1, which adsorbs approximately 10-20 % less, but it is moisture resistant comparable to

other adsorbents. And what is more, there is no drop of adsorption capacity of silica aerogels in the second adsorption/desorption cycle.

**Table 3:** Comparison of adsorption capacities of four different adsorbents used for removal of BTEX vapours from air.

Adsorbent	Adsorption capacity [g/100g]*							
	Benzene		Toluene		Ethylbenzene		Xylene	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2
TMOS1	95.91	104.41	91.14	99.82	93.98	81.97	102.54	106.50
TMES1	71.23	84.00	80.89	85.08	69.85	71.53	74.35	75.47
SG	65.39	66.55	64.64	60.48	64.85	51.68	64.12	57.83
AC	34.34	15.76	36.69	14.40	35.14	9.73	35.40	10.63

\* STDEV  $\leq$  2.

## CONCLUSION

The investigation of adsorption BTEX from air has shown that silica aerogel adsorbents are very efficient for the removal of BTEX vapours from waste gas streams. The possibility to tailor hydrophobicity and consequently moisture resistance of silica aerogel adsorbents and their repeated use in many adsorption/desorption cycles make them superior to conventional adsorbents as SG and AC. The improved performance of adsorption capacity by the hydrophilic silica aerogel based on TMOS over AC is higher for factor 3 and compared to SG it is almost doubled. The inclusion of MTMS precursor in standard sol-gel synthesis of silica aerogels greatly affects the adsorption properties. With higher amounts of MTMS used for the preparation of silica aerogels, aerogels become more hydrophobic, but specific surface area and consequently adsorption capacity decreases. On the other hand hydrophobic silica aerogel modified with TMES precursor has still very high specific surface area and due to this high adsorption capacity. Its capacity is approximately 20% lower compared to hydrophilic silica aerogel but its advantage is that it is moisture resistant, because moisture is ubiquitous in indoor environments and in many types of industrial gas streams and could alter the adsorption process.

All the above improvement factors significantly offset the costs, which would otherwise favour the use of conventional adsorbents for large-scale industrial BTEX trapping applications.

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