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Mesoporous silica functionalized with phenylamino and gluconamide groups: synthesis, characterization and use for sorption of diclofenac

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Synthesis of SBA-15 mesoporous organosilicas functionalized by phenylamino and gluconamide groups is reported. The organosilicas have been synthesized by co-condensation of proper monomers in the presence of Pluronic P123, and characterized by nitrogen sorption, X-ray diffractometry, elemental analysis, and FTIR spectroscopy to get detailed information about their porous structure, ordering and presence of introduced functional groups. The obtained materials were tested as sorbents of model pharmaceutical (diclofenac) to verify a potential application for removal of pharmaceutical: the observed static sorption capacities were ~50mg/g and ~130mg/g, for phenylamino- and gluconamide-functionalized samples, respectively, while for pristine sample no adsorption was observed.

1. INTRODUCTION

Mesoporous silica sorbents are widely used in many applications related to the removal of pollutants from water including heavy metals, dyes and pharmaceuticals. Outstanding properties of nanoporous silica materials such as high specific surface area, high pore volume, and well defined pores with adjustable sizes are very attractive particularly for the adsorption of biological molecules. The accessible pore size ranges are perfectly suited for many biomolecules such as drugs, vitamins, aminoacids, polypeptides, enzymes, and proteins. Moreover, silica mesoporous materials – opposite to polymeric and layered sorbents – do not swell in solutions.

In recent years some researchers have demonstrated usefulness of the functionalized ordered mesoporous silica (OMS) materials for adsorption of biomolecules. Zhao et al. demonstrated the use of modified SBA-15 materials for separation of proteins [1]. Balkus et al. showed that enzyme immobilization on MCM-41 silicas strongly depends on the molecule size [2]. In the case of peroxidase no adsorption was observed, indicating that the molecules were too large to entry into the 4 nm pores. Nanoporous silicas have been also tested as adsorbents of amino acids. For example, the adsorption of amino acids using MCM-41 materials was studied by Ernst et al. whose showed that sorption capacities strongly depends on the pH and nature of particular amino acids [3]. Deere et al. were the first to report adsorption isotherm of cytochrome c on different types of mesoporous materials [4]. Vinu et al. investigated the influence of the solution pH on the adsorption of cytochrome c [5, 6]. The applications of nanoporous silica-based sorbents for adsorption of small as well as large biological compounds have been nicely summarized [7–10].

The most popular ordered mesoporous silica materials is hexagonally ordered SBA-15 [11, 12], possessing thick pore walls and network of interconnecting micropores [13, 14]. SBA-15 materials are usually synthesized under strong acidic conditions by employing amphiphilic triblock copolymer Pluronic P123 via controlled hydrolysis and condensation of tetraethoxysilane (TEOS) followed by removal of polymeric template by either extraction with acidic ethanol or calcination at elevated temperatures. The SBA-15 are characterized by high specific surface, tunable pore diameters in the range of 4-30 nm and very high total pore volume reaching 2.5 cm^3/g. Possibility of OMSs modification by introduction functional groups into their framework or surface, makes these materials very attractive for sensing devices, catalytic and environmental applications [15–17]. Many papers have been devoted to the surface modification of these materials [18–21] to enrich the surface with wide range of chemical moieties for particular applications. Particularly, the presence of accessible functional groups on the silica surface can improve its sorption properties. Usually monomers like aminopropyltrialkoxysilane or mercaptopropyltrialkoxysilane are used to functionalize the surface layer and thus enhance adsorption properties. It seems very interesting to test other monomers form the wide range of potential surface modifiers. Co-condensation route seems to be very attractive as it affords to control simultaneously the surface and structural properties of the resulting materials. Thus, in this paper, two monomers bearing by phenylamino and propylgluconamide groups are used to synthesize SBA-15 mesoporous organosilicas via co-condensation route

2. EXPERIMENTAL

The following compounds were used: tetraethyl orthosilicate (TEOS, 98% Sigma-Aldrich), Pluronic 123 (P123, Sigma-Aldrich), hydrochloric acid (HCl, 36% POCH), nitric acid (HNO_3, 63% POCH), N-phenylaminomethyltriethoxysilane (PATS, ABCR), N-(3-triethoxysilyl)propylgluconamide (TPGA, 50%, Fluorochem), anhydrous ethanol (EtOH, 99.8%, POCH), diclofenac sodium salt (Sigma-Aldrich), deionized water (resistivity 18.2 MOhm cm). All chemicals were used as received, without further purification.

Synthesis of mesoporous SBA-15 organosilicas was performed according to [22–24]. In the model synthesis, 2 g of P123 was dissolved in 60 cm^3 of 2M HCl and 11 cm^3 of deionized water under vigorous stirring at 40°C. After 8h of stirring, 18 mmol of TEOS was added dropwise to this solution. After 60 minutes the 2 mmol of PATS (sample 2) or TMPD (sample 3) was added dropwise. The resulting mixture was stirred at 40°C for 24 h and aged at 100°C for next 48 h. The white solid was washed with deionized water, filtered and dried at 70°C. The template was removed by threefold extraction with the acidified EtOH at 70°C. For the comparative purposes also pristine silica sample was synthesized using 20 mmol of TEOS in the same regime.

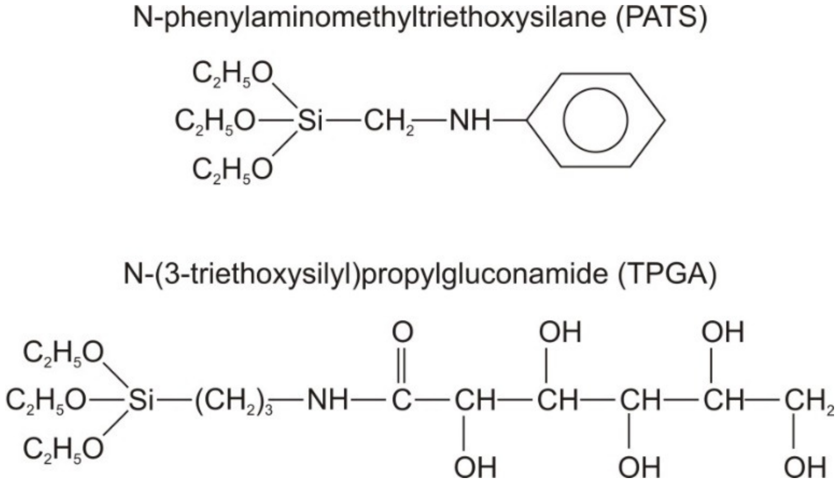
Nitrogen adsorption/desorption isotherms were measured at –196°C using an Quantachrome Nova 1200e analyser. All samples were degassed at 110°C in vacuum prior to measurements. BET specific surface areas (S_{BET}) were evaluated in the range of relative pressures p/p_0 of 0.05–0.20. Total pore volumes (V_p) were calculated by converting the amount adsorbed at p/p_0 ~0.99 to the volume of liquid adsorbate. Average pore sizes (d_{BJH}) were estimated using the BJH method. Powder X-ray diffraction (XRD) patterns were recorded using a Seifert RTG DRON-3 diffractometer (CuKα radiation) with 0.02° size step and 10s time step covering the range of $0.5° < 2\theta < 5.0°$ at RT. The CHN elemental analysis was carried out using the Perkin Elmer CHN 2400 analyser. Transmission

FTIR spectra were measured by means of VIR-200 spectrophotometer (Jasco).

The sorption capacity of diclofenac was examined the batch mode was used: ~5 mg of adsorbent was shaken with 5 cm^3 of diclofenac solution (250 mg/dm^3) at RT for 24 hours. The equilibrium adsorption amounts were calculated according to the formula: $a = (c_i - c) \cdot V/m$, where c_i is the initial diclofenac concentration (mg/dm^3), c is the equilibrium diclofenac concentration (mg/dm^3), V is the volume of the solution (dm^3) and m is the mass of the adsorbent (g). Measurements of diclofenac concentration were carried out using the UV-VIS spectrometer Specord 200 (Analitical Jena) at wavelength 279 nm.

3. RESULTS AND DISCUSSION

The formulas of the organosilica monomers (PATS and TPGA) are presented in Figure 1. As it can be seen, both monomers contains amide groups which may serve as potential binding sites.


N-phenylaminomethyltriethoxysilane (PATS)

N-(3-triethoxysilyl)propylgluconamide (TPGA)

Fig. 1. Structural formulas of the organosilica monomers used in this work

It is worth noting, that the TPGA monomer has a five hydroxyl groups which potentially act as adsorption sites. The TEOS/PATS and TEOS/TPGA ratio was chosen 18 mmol:2 mmol. Such a ratio assures that significant (although not high) number of functional groups will be attached to the inorganic silica network formed by TEOS. Form the other hand, the degree of ordering should not be decreased significantly due to the (i) low co-monomer amount and (ii) applied prehydrolysis of TEOS (1 hour) which let to build silica mesophase around the micelles of Pluronic P123 which is not influenced by organosilicas bulky molecules.

Nitrogen isotherms of all samples are presented in Figure 2. All three isotherms are characteristic for SBA-15 mesoporous materials i.e. have a sharp hysteresis loop, reflecting capillary condensation of adsorbate in the uniform mesopores channels, and evaporation step related to the evacuation of adsorbate from the pores.

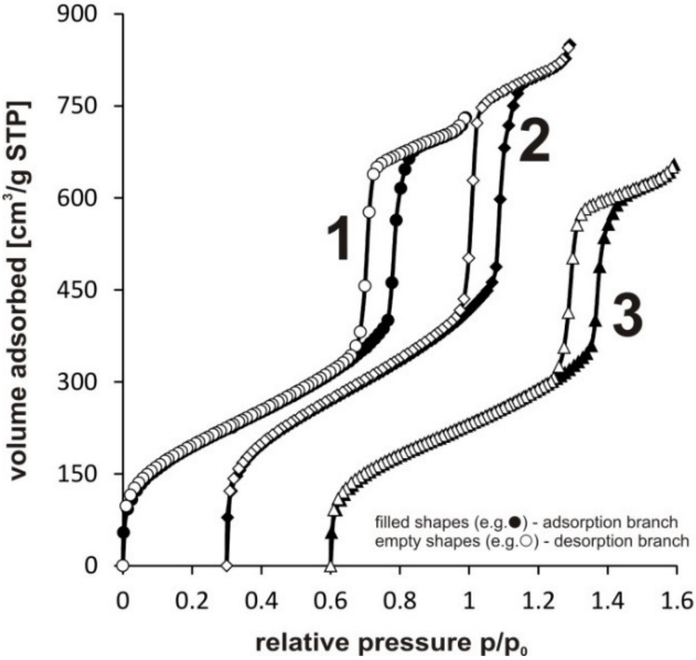


Fig. 2. Nitrogen sorption isotherms of the samples studied (1 – TEOS, 2 – TEOS:PATS, 3 – TEOS:TPGA).

The isotherms of the samples studied exhibit hysteresis loops which is attributed to the presence of mesopores in the material. Those loops can be classified as belonging to the type H1. The sharpness of the adsorption and desorption branches testifies to a narrow mesopore size distribution. Thus, it can be concluded that the framework of the obtained materials is composed of an array of uniform mesopores with the same diameter. However, it should be noted that also micropores are present, what is manifested by the sudden increase of the amount of adsorbed nitrogen in the range of relative pressures in the range 0–0.1. The presence of micropores is a result of a penetration of the silica networks by hydrophilic poly(ethylene glycol) chains of the Pluronic P123 template during the synthesis.

The parameters of porous structure derived from the isotherms using appropriate models are summarized in Table 1. All materials exhibit high values of surface area (S_{BET}) ranging from 726 to 871 m^2/g; the highest value of S_{BET} has the phenylamino-functionalized sample 2. Pore volumes (V_p) and diameters (d_{BJH}) do not differ significantly among the samples investigated, except sample 2, which has noticeably higher values of V_p and d_{BJH}. The micropore volumes (V_{micro}) of the samples 1 and 3 are similar, but in the case of sample 2 it is two times higher indicating higher content of microporosity. The sample 2 is also characterized by much larger mesopores (9.8 nm) than the samples 1 and 3 (4.9 nm and 4.6 nm, respectively). It is clear that even very small amount of PATS can strongly affect the porous structure of the forming SBA-15 organosilica, even if the co-condensation rate is low (*vide infra* - results of elemental analysis). In my previous unpublished results, the strong effect of PATS addition on porosity of the final materials have been always observed.

Table 1. Structural parameters derived from nitrogen sorption isotherms of the samples studied.

sample	molar composition [mmol]	nitrogen sorption data			
		S_{BET} [m^2/g]	V_p [cm^3/g]	V_{micro} [cm^3/g]	d_{BJH} [nm]
1	TEOS (20)	726	1.13	0.16	4.9
2	TEOS:PATS (18:2)	871	1.31	0.37	9.8
3	TEOS:TPGA (18:2)	668	1.01	0.15	4.6

XRD diffractograms (not given here) reveal a typical SBA-15 pattern of signals. Three well-resolved peaks are observed: sharp reflection in the range of $2\Theta \approx 0.8–1.2$, which corresponds to the plane 100 and two well resolved signals of lower intensity at $2\Theta \approx 1.5–1.8$, corresponding to planes 110 and 200. This allows to assign it to the hexagonal space group p6m, testifying to the mesoscopic ordering of the obtained samples. However, in the case of the samples 2 and 3, 110 and 200 signals are less pronounced, testifying that the addition of organosilica monomers diminishes the degree of ordering. In this case, it is not drastically decrease because only 10 molar % of the co-monomer was added to the TEOS during the synthesis.

Elemental analysis confirms that the co-condensation of both monomers was successfully achieved, although it was not quantitative. In the case of the sample 2, the theoretical content of nitrogen is 1.81% while elemental analysis revealed that only one fourth of nominal nitrogen amount is present in the final sample. Of course, it should be realized that in the final materials also the unremoved template (Pluronic P123) is present (carbon content in pure silica sample 1 is ~4%). But even taking into account this fact, the conclusion is that only ~25% of PATS monomer is distributed in final material. In the case of the sample 3, the co-condensation efficiency is higher but careful analysis of the elemental analysis data shows the following: theoretical carbon content in the sample 3 (10.5%) is much higher value than observed one (6.36%). In opposite, theoretical nitrogen content (1.35%) is lower than the observed one (1.83%). This may lead to the conclusion that a fraction of gluconamide chains is broken on the course of the synthesis leaving the amide groups attached to the silica skeleton and polyhydroxy parts are removed. Is should be clearly stated here, that – at this stage – this is only a speculative hypothesis and further investigations must be done to clarify the observed discrepancies between theoretical and observed elemental compositions.

Table. 2. CHN elemental analysis of the samples studied.

sample	Molar composition (mmol)	Elemental data			Theoretical content of C	Theoretical content of N
		%C	%H	%N		
1	TEOS (20)	4.15	2.02	0.00	0.00	0.00
2	TEOS:PATS (18:2)	5.18	1.96	0.41	10.88	1.81
3	TEOS:TPGA (18:2)	6.36	2.53	1.83	10.47	1.35

FTIR spectra of the samples 1-3 are very similar and are presented in Figure 3. A characteristic feature is the presence of the most intensive and wide absorption band in the region of 1000–1150 cm^{-1}. This intensive band is definitely attributed to stretching modes of the siloxane framework [25]. Band at ~800 cm^{-1} corresponds to bending modes of siloxane fragments.

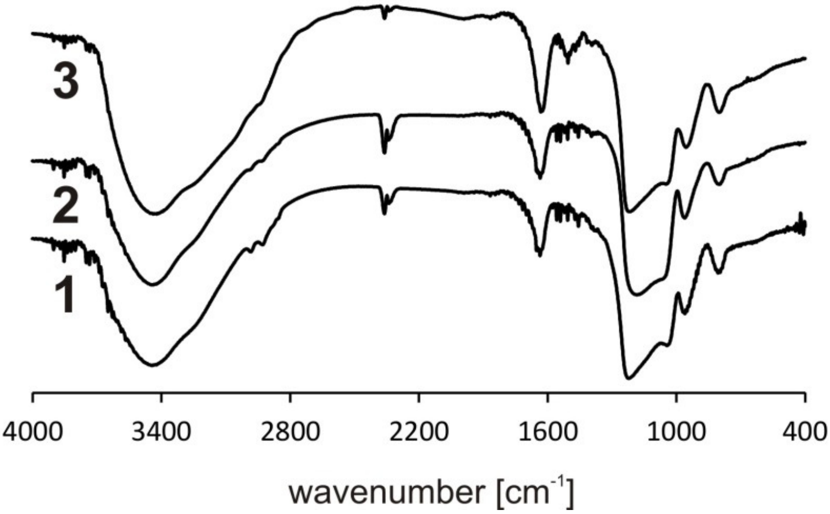


Fig. 3. FTIR spectra of the samples studied

In all spectra a very wide and intensive band, that extends from ~3700 cm^{-1} to ~2800 cm^{-1} is observed. It arises from the stretching mode of the physically adsorbed water. In the case of the sample 3 this band is more intensive than in the case of the samples 1 and 2, what can indicate more water adsorbed on the surface due to hydrogen bonds which might be formed between water molecules and hydroxy groups present in gluconamide fragments of the sample 3. Silanol groups can also takes part in the formation of hydrogen bonds, however in the case of the sample 3, the first effect is probably predominant. In addition the presence of physically adsorbed water is confirmed by medium-intensity band somewhat at ~1630cm^{-1} that corresponds to water bending vibrations – it can be seen than it the case of the sample 3 this band is more intensive than in the case of the samples 1 and 2. The presence of the CH_2 links present in the residual Pluronic P123 (and also propyl chains of PATS), is indicated by a group of absorption bands in the region 3000–2850 cm^{-1}, corresponding to stretching vibrations of CH fragments.

The bands characteristic for the presence of aromatic rings (sample 2) cannot be found due to the low amount of co-condensed PATS (~30%), thus poor incorporation of benzene rings in the silica framework. The same is true with the amide groups, thus the corresponding signals of stretching vibrations of secondary amines (normally located at 3300-3500 cm^{-1}) are masked by the band of physically adsorbed water.

To verify the potential sorption applications of the obtained SBA-15 organosilicas, diclofenac was chosen as a model drug to be adsorbed. Diclofenac is classical non-steroidal anti-inflammatory drug used in high amounts worldwide. Despite the fact that diclofenac itself is phytotoxic only in concentrations above those occurring nowadays, products of its photo degradation can have much higher toxicity. On the basis of previous research concerning adsorption of diclofenac on silica-based materials, the optimal pH for adsorption experiments was fixed as 6. The observed values of static sorption capacities obtained using single solution of diclofenac (250 mg/dm^3) were the following: sample 1–0.6 mg/g, sample *2* – 49.4 mg/g, sample 3 – 128.9 mg/g. For pure silica sample 1 no adsorption was observed what means that the crucial role in the adsorption of diclofenac is played by the surface functionalities introduced by co-condensation of TEOS with PATS and TPGA. The hydroxyl groups present in the gluconamide chain (sample 3) can serve as potential binding sites for diclofenac; however there is a competition between drug and water molecules, so probably amide groups are rather responsible for drug binding to the surface, as in the case of the sample 2.

4. CONCLUSIONS

Mesoporous SBA-15 organosilicas functionalized with with phenylamino and gluconamide groups has been synthesised and characterized. The materials have well-developed mesoporosity and considerable amount of microporosity as well as mesoscopic ordering. Elemental analysis confirms successful (although not full) incorporation of the PATS and TPGA in the final materials

The observed values of static sorption capacities are ~50 mg g^{-1} for PATS- and 130 mg g^{-1} for TPGA-functionalized material. In opposite, for pure-silica sample no adsorption was observed, which confirms the crucial role played by surface functionalities in the sorption of diclofenac. The initial results presented in this article testify to the usefulness of the obtained materials towards removal of diclofenac (and more probably a wider range of pharmaceuticals) form waters and wastewaters.

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Mariusz Barczak was born in Świdnik in Poland in 1978. After graduation from the Faculty of Chemistry, Maria Curie-Skłodowska University in 2004, he was employed in the Department of Theoretical Chemistry as an assistant. In 2007 he obtained Ph.D. degree on the basis of desideration entitled: *"Synthesis, characterization and adsorption properties of bridged polysilsesquioxanes functionalized with amine and thiol groups"*. Since 2007 he has been held a position of adjunct at the same University. He is a co-author over fifty original scientific papers. His scientific interest are synthesis and functionalization of porous materials as well as their applications for removal of pollutants from the environment, controlled drug delivery systems and as chemical sensors.