

Summary of PhD thesis

**Synthesis of functionalized silica aerogels and evaluation of their
application fields**

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I. INTRODUCTION AND OBJECTIVES

Silica aerogels are among the lowest density solids in the world, and possess a number of special properties such as extremely high specific surface area (500-1200 m²/g) and porosity (80-98.9%), as well as ultralow electric, sound and thermal conductivity. Aerogels also show remarkable compressive strengths compared to their outstandingly low density. Due to these interesting characteristics, aerogels found applications as insulating materials of buildings and spacecrafts, as well as in the detection of high energy particles and in the collection of cosmic dust particles.

In the last three decades, aerogels attracted considerable attention in the field of materials science. However, only a few researches were focused on their chemical modification (functionalization) and the effects it has on their properties. Due to their synthesis method (sol-gel technology), aerogels can be functionalized with a great variety of organic side chains and complexing agents. Both the physical and the chemical characteristics of the as-prepared new materials significantly differ from those of the unmodified ('natural') aerogels. Thus, functionalized aerogels may find applications in completely new fields.

Our group at the Department of Inorganic and Analytical Chemistry (University of Debrecen) have been conducting researches in the field of preparing and characterizing aerogels and aerogel composites for more than a decade. Upon joining the group, I started my doctoral work by setting two main aims. My primary objective was to synthesize new, chemically modified aerogels, as well as to characterize their structures, compositions and morphologies. Since functionalized aerogels have only found very limited use so far, my second aim was the exploration of some of the potential application fields of the newly prepared materials. Thus, part of the new aerogels were tested as novel type of high pressure liquid chromatographic (HPLC) stationary phases, others as inorganic fillers of poly(methyl methacrylate) (PMMA), and the ones modified with catalytically active functional groups were evaluated as catalysts.

II. EXPERIMENTAL METHODS

Characterization

Nitrogen adsorption/desorption porosimetry measurements were carried out using a Quantachrome Nova 2200e type surface area and porosity analyzer. Approximately 20 mg of ground aerogel samples were used, that were outgassed at 100 °C for 24 hours prior to the measurements.

Scanning electron microscopy (SEM) studies were performed by a Hitachi S-4300 instrument equipped with a Bruker energy dispersive X-ray spectroscope. The monolithic aerogel samples of approximately 2-4 mm sizes were embedded in a low melting point alloy (Wood's metal). All surfaces were covered by a sputtered gold conductive layer. 5-10 kV accelerating voltage was used for the high resolution images.

Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus FT-IR Spectrometer. All samples were prepared as KBr diluted pellets.

Nuclear magnetic spectroscopy (NMR) measurements were carried out with a Bruker AM 360 spectrometer.

Chromatographic experiments

HPLC measurements were performed by a Jasco chromatograph equipped with an ERC 3315 degassing module, a Jasco LG-980-02 low-pressure gradient valve unit, a Jasco PU-980 pump, a Jasco AS-1555 autosampler, a Jasco UV-975 UV-VIS detector and Jasco ChromPass software.

Characterization of aerogel-PMMA composites

Shore D hardnesses were determined on the basis of the EN ISO 868:2003 standard. We measured the instantaneous hardness with a D type durometer. As the next step, we executed compression tests based on the standard ISO 604:2003 using an Instron 8874 servohydraulic material testing machine. Impact strengths were determined by a custom-made miniature falling dart impact tester of Gardner's type, equipped with an anti rebound device.

Simulated body fluid (SBF) solution was freshly made using $(\text{HOCH}_2)_3\text{CNH}_2$, NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 , NaHCO_3 , and K_2HPO_4 . The pH was set to 7.40 ± 0.02 by 0.1M HCl solution. *In vitro* bioactivity studies were performed by soaking freshly fractured smaller composite specimens in 4 ml volume of SBF test solution in completely filled-up and sealed sample vials kept at 37 °C in an incubator for 20 days. Afterwards, the surfaces were studied with SEM technique.

Catalytic tests

Catalytic performances of CuAM12 and CuAM14 aerogels was evaluated by the oxidation of phenol with hydrogen peroxide, in aqueous media. The concentration of phenol was monitored by HPLC. Phenomenex Lichrosphere 5 RP-18e (4.6mm×150 mm, 5 µm) was used. The applied eluent was 40% methanol – 60% potassium dihydrogen phosphate (0.025 mM) / phosphoric acid (0.52 mM) buffer (pH 4). The wavelength of detection was typically 254 nm. 20 µl of sample was injected.

Mass spectrometric (MS) measurements were performed by MicroTOF-Q type Qq-TOF MS instrument equipped with an electrospray ion source (ESI) where the spray voltage was 3 kV. Nitrogen was utilized as drying gas. The drying temperature was 180 °C and the flow rate was 4.0 L/min. Mass spectra were recorded by means of a digitizer at a sampling rate of 2 GHz and evaluated with the DataAnalysis 3.4 software from Bruker.

III. NOVEL SCIENTIFIC ACHIEVEMENTS

1. The syntheses of new types of chemically modified aerogels were carried out for the first time, as well as the characterization of their morphologies and structures.

1.1. A synthesis method for the preparation of aerogels functionalized with (3-glycidoxy)-propyl- (Si-Gly) and hexadecyl- (Si-C16) groups, as well as with Kryptofix[2.2] (Si-Kry), [cyclen-Cu]- and [cyclam-Cu]-complexes (CuAM12 and CuAM14) was developed for the first time.

The aerogels (Figure 1.) were synthesized using a modified base-catalyzed sol-gel method. First, two solutions were prepared (Solution-A and Solution-B). Solution-A contained the

2.1. Aerogel based HPLC columns were prepared for the first time.

First, aerogels were ground and sieved. The average diameter of the obtained aerogel particles were around 25-125 μm . In the next step, the aerogels were loaded into conventional stainless steel HPLC columns by the slurry method. The stationary phases were densified with the help of an HPLC pump, and the conditioned with the appropriate eluents.

2.2. The basic chromatographic properties of the novel aerogel-based stationary phases was studied. It can be concluded, that they allow the separation of 2-5 analytes.

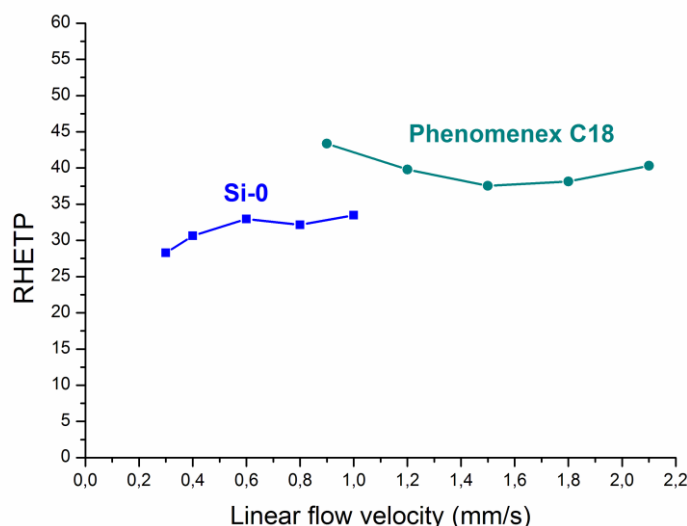


Figure 2. Reduced theoretical plate heights (RHETP) of Si-0 aerogel column and Phenomenex C18 (5 μm particle diameter) column. Separation conditions: Si-0: hexane: absolute ethanol=90:10 eluent, 0.3-1.0 ml/min flow velocity. Phenomenex C18: water:methanol=55:45 eluent, 0.4-1.2 ml/min flow velocity.

Experiments revealed, that while Si-0, Si-Gly és Si-Kry columns exhibited normal phase behavior, Si-C16 functioned as a reversed phase. In isocratic mode, baseline separation of generally two or three analytes could be achieved, while in gradient mode, in one case (Si-C16), five analytes were separated. A significant peak broadening could be observed in each chromatogram, which is certainly stemming from mass transfer resistance that arises inside the oversized aerogel particles.

2.3. It was found, that ideal separation conditions require the application of eluent flow rates well under 1.0 ml/min, as well as the use of submicron sized particles.

In an attempt to determine the ideal separation conditions, the effect of eluent flow velocity on theoretical plate heights was studied. The obtained van Deemter plots show that the optimal flow rate is well under 0.3 ml/min. Taking peak broadening into consideration as well, it can be concluded that besides ultralow flow rates, submicron particle sizes are also needed in order to improve mass transfer kinetics.

2.4. For comparison purposes, the reduced theoretical plate heights of an aerogel-based column and a commercially available Phenomenex C18 column (5 μm particle diameter) were evaluated. It was revealed, that the advantageous features stemming from the special structure already show under non-optimal separation conditions (such as overtly large particle diameters and eluent flow velocity).

Comparison of the Si-0 aerogel column and the Phenomenex C18 HPLC column is only possible by calculating the RHEPT values. RHETP values can be obtained by dividing the theoretical plate heights with the mean particle diameter. Thus, columns of different particle sizes become comparable. Results are shown in Figure 2. It can be seen, that RHETP values are quite similar despite the huge difference in particle diameters (25-125 μm for Si-0, and 5 μm for Phenomenex C18.) This implies, that the efficiency of the aerogel-based column is acceptable despite separation conditions far from the ideal.

3. Natural and functionalized ground aerogels (Si-0, Si-0_{500°C}, Si-C16 and Si-Ph) were tested as fillers of PMMA composites prepared by *in situ* free radical bulk polymerization for the first time.

3.1. A synthesis method for the preparation of homogenous, bubble-free PMMA-aerogel composites was developed.

Composites were prepared by free-radical bulk polymerization, using cumene hydroperoxide catalyst and N,N-trimethylaniline redox-pair. Freshly distilled methyl methacrylate was used, and the reaction was carried out at 60 °C and ambient pressure, under inert (nitrogen) atmosphere. Prior to synthesis, ground aerogels were outgassed at 100 °C under dynamic vacuum for 30 minutes.

3.2. It was evidenced, that aerogels as fillers enhance the mechanical properties of PMMA.

To characterize the mechanical properties of the composites, Shore D hardnesses, as well and compressive and impact strengths were determined. Surprisingly, it was found that Shore D hardnesses and compressive strengths increased in all cases, while impact strengths were only enhanced by functionalized aerogels. This reinforcing effect is remarkable considering the low aerogel contents of the composites (4-9 m/m%) and the very low compressive strengths of monolithic silica aerogels (~0.01 MPa).

3.3. It was revealed, that upon soaking PMMA-aerogel composites in SBF, the aerogel contents of certain composites dissolve, leaving porous, spongy surfaces behind.

SBF is widely used for the evaluation of the biocompatibilities of bone cements and artificial joint implants. PMMA-aerogel composites were soaked in SBF for 20 days. Afterwards, surfaces were studied with SEM technique. It was revealed, that in the cases of Si-C16 and Si-0, the aerogel content dissolved, and thus a highly porous surface developed.

4. Aerogels functionalized with tetraaza-macrocyclic (cyclen and cyclam) Cu(II) complexes were evaluated as catalysts for the first time.

4.1. It was found, that upon covalently bonding the complexes to the aerogel surface, an increase in efficiency was achieved. Based on the control experiments using the free complexes in the homogenous phase, seven- and fifteen-fold increase in performance was measured for CuAM14 and CuAM12, respectively. The phenomenon can be explained by the so-called confinement effect.

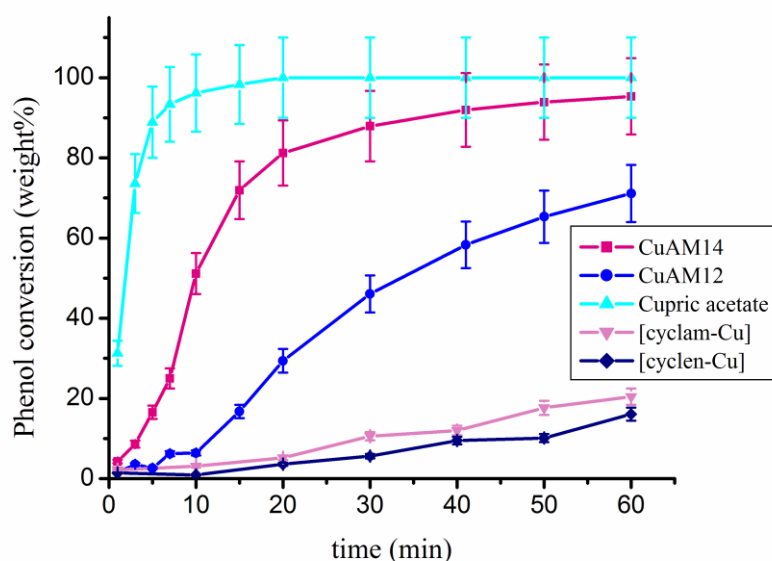


Figure 3. Kinetic curves representing the progress of phenol conversion over time with the aerogel catalysts CuAM12 and CuAM14, as well as the free macrocyclic complexes [cyclam-Cu] and [cyclen-Cu], and cupric acetate at 70 °C.

As a model reaction, the oxidation of phenol with hydrogen peroxide was chosen. For comparison purposes, the catalytic tests were also performed in the homogenous phase, using the free complexes and free Cu(II) ions. While the free complexes, [cyclen-Cu] and [cyclam-Cu] showed a rather poor activity (oxidizing only 16 and 21% of the total phenol content in 60 minutes, respectively), in the cases of CuAM12 and CuAM14 95 and 71% of phenol was degraded, respectively. In order to make catalytic performances even more comparable, we estimated the rates of phenol degradation by simple linear regression. Fitting was performed through a set of points selected from the initial linear segments of the kinetic curves. The calculated turnover frequencies for CuAM14 and CuAM12 are ca. 15 and 7 times higher than that of free [cyclam-Cu] and [cyclen-Cu] complexes in the homogeneous phase, respectively.

4.2. Oxidation products were identified by ESI-MS technique. It was revealed, that the oxidation mechanism includes quinone formation, followed by ring opening and stepwise oxidation and degradation steps, which finally lead to a mixture of biodegradable and environmentally friendly short-chained carboxylic acids.

Based on the experiments, it can be concluded that under the applied reaction conditions, after 240 minutes, no toxic compounds can be found in the solutions, only some short-chained carboxylic acids such as acrylic acid, malonic acid, maleic acid, succinic acid and oxalic acid.

4.3. The reusability of the aerogel catalysts was studied. It was found, that both aerogels preserved their activity even after four complete reaction and separation cycles. However, decrease in the catalytic performance was observed in both cases. For CuAM14, the decrease stopped at ca. 50% conversion rate in the third cycle, while this value was only 15% for CuAM12 in the last cycle.

There are several possible explanations for the decrease in the catalytic performance. Most likely, oxidation byproducts adsorb on the aerogel surface, gradually blocking the active sites. This theory is supported by the observation of the color change of the catalyst, which

intensified in the forthcoming cycles. Additionally, moderate solubility of the amorphous silica aerogel skeleton in water may also contribute to the effect.

IV. POSSIBLE APPLICATIONS OF THE RESULTS

During my research, I synthesized new types of functionalized aerogels, and tested their eligibility in fields in which they have never been tested before. Results show, that functionalized aerogels might find application in analytical or polymer chemistry. Chromatographic experiments show, that aerogels could be used as novel stationary phases in supercritical fluid chromatography. On the other hand, aerogels significantly improved the mechanical properties of PMMA composites, and furthermore, a porous surfaces can be developed if needed. These attributes make PMMA-aerogel composites ideal candidates as advanced bone cements or as wear and heat resistant polymer composites for demanding technical applications. On the other hand, aerogels as catalysts seem to be less promising. Although efficiencies are remarkably high at the beginning due to the confinement effect, these quickly deteriorate due to poor reusability. In order to overcome these preliminary setbacks, further research is needed.

LIST OF PUBLICATIONS

Publications related to the PhD thesis:

1. I. Lázár, H. F. Bereczki, S. Manó, L. Daróczy, Gy. Deák, I. Fábián, Z. Csernátony. Synthesis and study of new functionalized silica aerogel poly(methyl-methacrylate) composites for biomedical use. *Polymer Composites* 36 (2) **2015** 348-358.
Impact factor (2015): 2,008
2. H. F. Bereczki, L. Daróczy, I. Fábián, I. Lázár. Catalytic activity of silica aerogels functionalized with Cu(II) complexes of cyclen and cyclam. *Microporous and Mesoporous Materials* 234 **2016** 392-400.
Impact factor (2016): 3,349

Oral presentations related to the PhD thesis:

1. Bereczki H. F., Lázár I. Aerogels as novel liquid chromatographic stationary phases. „XXXII. Kémiai Előadói Napok Tudományos Szimpózium”, 25-27th October 2010, Szeged, Hungary
2. Bereczki H. F., Kuttor A., Lázár I., Fábián I. Functionalized silica aerogels as novel liquid chromatographic stationary phases. „MTA Szervetlen és Fémorganikus Kémiai Munkabizottság és az MTA Anyag- és Molekulaszerkezeti Munkabizottság előadói ülése” 24-26th March 2011, Demjén, Hungary
3. Bereczki H. F., Kuttor A., Lázár I., Fábián I. Liquid chromatographic applications of silica aerogels. „Magyar Kémikusok Egyesülete I. Nemzeti Konferencia”, 22-25th May 2011, Sopron, Hungary
4. Bereczki H. F., Lázár I., Manó S., Daróczy L., Deák Gy., Fábián I., Csernátony Z. Synthesis and characterization of poly(methyl methacrylate)-functionalized silica aerogel composites, and their dissolution in simulated body fluid. „XXXIV. Kémiai Előadói Napok Tudományos Szimpózium”, 2-4th November 2011, Szeged, Hungary

Conference posters related to the PhD thesis:

1. H. F. Bereczki, I. Lázár, Gy. Deák, S. Manó, L. Daróczy, I. Fábián, Z. Csernátony. Functionalized silica aerogel-poly(methyl methacrylate) composites for potential use in bone cements. *International Conference on Bioinspired and Biobased Chemistry and Materials*, 3-5th October 2012, Nice, France
2. H. F. Bereczki, N. Linares, J. García Martínez, I. Fábián, I. Lázár. Mesoporous silicas functionalized with macrocyclic copper(II) complexes and their use as catalysts. *4th International Conference on Multifunctional, Hybrid and Nanomaterials*, 9-13th March 2015, Sitges, Spain



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List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

1. **Bereczki, H. F.**, Daróczy, L., Fábán, I., Lázár, I.: Sol-gel synthesis, characterization and catalytic activity of silica aerogels functionalized with copper(II) complexes of cyclen and cyclam. *Microporous Mesoporous Mat.* 234, 392-400, 2016. ISSN: 1387-1811.
DOI: <http://dx.doi.org/10.1016/j.micromeso.2016.07.026>
IF: 3.349 (2015)
2. Lázár, I., **Bereczki, H. F.**, Manó, S., Daróczy, L., Deák, G., Fábán, I., Csernátó, Z.: Synthesis and study of new functionalized silica aerogel poly(methyl methacrylate) composites for biomedical use. *Polym. Compos.* 36 (2), 348-358, 2015. ISSN: 0272-8397.
DOI: <http://dx.doi.org/10.1002/pc.22949>
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The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of Web of Science, Scopus and Journal Citation Report (Impact Factor) databases.

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