Elaboration and characterization of organic/inorganic hybrid nanoporous material incorporating Keggin-type Mo-Si polyanions

T. Dizhbite¹, N. Mironova-Ulmane², A. Volperts, A. Andersone¹, L. Jashina¹, T. Kärner³ and G. Telysheva¹

¹Latvian State Institute of Wood Chemistry, Riga, Latvia
²Institute of Solid State Physic, University of Latvia, Riga, Latvia
³Institute of Physics, University of Tartu, Tartu, Estonia

E-mail: ligno@edi.lv

Abstract. A novel nanoporous (pore size of 11 nm in average, BET surface area of 30 m²/g, pore volume of 300 mm³/g) hybrid inorganic-organic material was synthesized using the solid-phase interaction at room temperature of plant-originated phenylpropanoid polymer lignin and a Keggin-type heteropolyanion [SiMo₁₂O₄₀]⁴⁻. The partly reduction of Mo(VI) to Mo(V) and complexes formation between lignin and polyanion have been established by EPR, FT-IR and Raman spectroscopy. The XRD pattern and FT-IR spectrum of the hybrid material and indicates that [SiMo₁₂O₄₀]⁴⁻ anion maintains the Keggin structure.

1. Introduction

Organic/inorganic hybrids are a relatively new type of materials with interesting optical, electrical and thermal properties [1,2]. Polyoxometalates (POMs), nanosized metal–oxygen macroanions are suitable building blocks of nano-structures hybrid materials in combination with organic donor molecules, surfactants and polymeric substrates due to their potential applications in such fields as bifunctional catalysis, magnetic nanoparticles, energy transfer, luminescence and antiviral chemotherapy [3,4]. Among POMs, the Keggin polyanions are attractive as the inorganic precursors owing to their reactivity towards organic groups [5]. Silicomolybdate polyoxometalate, [SiMo₁₂O₄₀]⁺⁺⁺⁺, contains biologically active Si and Mo elements and forms nanosized POM clusters that are of interest in bioanalysis, material science, catalysis, surface modification, and ecology [6]. Use of plant polymer matrices with their natural nanoscale organization as host components for hybrids design opens new possibilities for tailored materials obtaining [7]. Lignin, the second most abundant biopolymer after cellulose, is characterized with developed π-conjugated aromatic structure, hydrophobic properties, high inclination to electron donation, charge transfer complexing and supramolecular association. Isolated from plant tissue lignins are available in large quantities as by-products from lignocellulosic biomass chemical processing, e.g. pulp or ethanol production.

The present work was carried out with the aim to develop further the elaboration of multifunctional hybrid materials based on the lignin and [SiMo₁₂O₄₀]⁺⁺⁺⁺. For the first time the synthesis of such a hybrid was reported in 2006 [8].

The materials with different silicomolybdate polyanions loadings were synthesized using a solvent-free mechanochemical treatment at room temperature and characterized by powder X-ray diffraction,
nitrogen gas adsorption-desorption, thermogravimetry, EPR spectroscopy, FT-IR spectroscopy and Raman microscopy.

2. Experimental

The hybrid materials with different polyanions loadings (molar ratio SiMo$_{12}$O$_{40}$:lignin = 1:4 and 1:16) were obtained using a solvent-free mechnochemical synthesis involving the intimate mixing of heteropolyanion crystals with quaternized lignin followed by irradiating by ultrasound at room temperature. Preparation of parent compounds, H$_4$SiMo$_{12}$O$_{40}$ and quaternized lignin, was described in the previous paper [8]. X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with CuK$_\alpha$ radiation ($\lambda$ = 1.5418 Å). The XRD pattern for siliconolybdate prepared (figure 1A) coincided well with the known structure of H$_4$SiMo$_{12}$O$_{40}$·13H$_2$O [9] with the crystal data P1, a = 14.096(1) Å, b = 13.499(1) Å, c = 13.976(1) Å, $\alpha$ = 109.3(1)$^\circ$, $\alpha$ = 119.1(1)$^\circ$, $\gamma$ = 67.8(1)$^\circ$, V = 2115.74 Å$^3$.

Parameters of porous structure of the samples in terms of BET specific surface area, pores volume and pore size distribution were calculated from the nitrogen gas adsorption-desorption isotherm determined at 77K using a KELVIN 1042 sorptometer.

Thermogravimetric analysis (TGA) was carried out in air on a MOM Q-Derivatograph within the range 20-1000 °C with a heating rate of 10 °C/min.

IR spectra of the samples were obtained at room temperature with a Spectrum One (Perkin Elmers) FT-IR spectrometer using standard KBr pellet technique. Measurements were taken in the wavenumbers range of 4000-400 cm$^{-1}$, with a resolution of 4 cm$^{-1}$ and scan number of 64. For assignment of the characteristic bands the Faix classification for lignin [10] and the data of [11] for H$_4$SiMo$_{12}$O$_{40}$ were used.

Figure 1. XRD patterns of pure siliconolybdate (A) and the product (B) of its interaction with quaternized lignin at the co-reagents molar ratio 1:4 (B).

The Raman spectra were obtained at room temperature using 3D scanning confocal microscope with spectrometer Nanofinder-S (SOLAR TII, Ltd.) and the He-Cd laser (441.6 nm, 50 mW cw power) as excitation source [12]. The laser power at the sample was regulating by the neutral filter (OD=0.5) to prevent sample heating. The measurements were performed through Nikon Plan Fluor 40x (NA=0.75) objective, mounted on inverted Nikon ECLIPSE TE2000-S optical microscope. The elastic component of laser light was eliminated by the edge filter. The Raman spectra were recorded by a TE cooled back-thinned CCD camera (ProScan HS-101H) attached to the monochromator-spectrograph Model MS5004i (SOLAR TII, Ltd., focal length 520 mm, 600 grooves/mm grating, a resolution 0.16 nm).
The EPR spectra were recorded using an EMX-6/1 spectrometer (BRUKER) working at X-band frequency with 100 kHz modulation. Magnetic field varied between 100 and 7000 Gauss. Measurements were made in the temperature range 10K – 293K.

3. Results and Discussion
Comparison of XRD patterns of the parent silicomolybdate and the product of its interaction with quaternized lignin (figure 1 A and B, respectively) showed lower crystallinity of the hybrid resulting from the distribution of $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ polyanion inside amorphous lignin matrix. Nevertheless, the peaks presented in the XRD pattern of the hybrid indicate that also in this case $\text{SiMo}_{12}\text{O}_{40}^{4-}$ anion retains the Keggin structure.

In accordance with TGA data obtained the beginning of thermal degradation was observed at 200°C for quaternized lignin and at 270°C for the hybrid lignin-$[\text{SiMo}_{12}\text{O}_{40}]^{4-}$. This increase suggests strong organic-inorganic phase interactions that sufficiently influence thermal resistance.

Table 1. The characteristic adsorption bands in FT-IR spectra of the parent compounds and $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ - lignin hybrids.

| Sample | Wavenumber, cm$^{-1}$ | Assignment |
|--------|------------------------|-------------|
| POM    | 956                    | Mo=O terminal |
|        | 908                    | Si=O         |
|        | 859                    | Mo-O-Mo, angle sharing bridge |
|        | 778                    | Mo-O-Mo, edge sharing bridge |
| Quaternized lignin | 1617 | C=O, conjugated |
|        | 1472 | C-H asymmetric deformation in CH$_2$ and CH$_3$ |
|        | 1514 | C=C stretching of the aromatic ring |
|        | 1416 | C=O in carboxylate ions |
|        | 1266 | C-O in carboxylic acids |
|        | 1142 | Aromatic C-H in plane deformation |
|        | 1049 | C(alkyl)-O(ether) |
| Product of solid-state H$_4$$\text{SiMo}_{12}\text{O}_{40}$·13H$_2$O – quaternized lignin interaction (1:4) | 1634 | C=O, conjugated |
|        | 1472 | C-H asymmetric deformation in CH$_2$ and CH$_3$ |
|        | 1266 | Guaiacyl ring breathing |
|        | 1142 | Aromatic C-H in plane deformation |
|        | 1032 | C(alkyl)-O(ether) |
|        | 952  | Mo=O terminal |
|        | 905  | Si=O |
|        | 867  | Mo-O-Mo, angle sharing bridge |
|        | 798  | Mo-O-Mo, edge sharing bridge |
| Product of solid-state H$_4$$\text{SiMo}_{12}\text{O}_{40}$·13H$_2$O – quaternized lignin interaction (1:16) | 1635 | C=O, conjugated |
|        | 1602 | C=C stretching of the aromatic ring |
|        | 1512 | C=C stretching of the aromatic ring |
|        | 1472 | C-H asymmetric deformation in CH$_2$ and CH$_3$ |
|        | 1420 | C=O in carboxylate ions |
|        | 1266 | Guaiacyl ring breathing |
|        | 1142 | Aromatic C-H in plane deformation |
|        | 1031 | C(alkyl)-O(ether) |
|        | 870  | Mo-O-Mo, angle sharing bridge |
|        | 950  | Mo=O terminal |
|        | 904  | Si=O |
|        | 797  | Mo-O-Mo, edge sharing bridge |
The absorption bands observed in FT-IR spectra of the hybrids synthesized and the corresponding parent compounds are listed in the Table 1. In the spectrum of pure silicomolybdate the main peaks at 956, 908, 859 and 778 cm\(^{-1}\), characteristic for a Keggin-type heteropolyanion, were found. In the spectra of hybrid products bands belonging to lignin and \([\text{SiMo}_{12}\text{O}_{40}]^{4-}\) both are visible. With the increase of lignin content in hybrid material intensity of lignin peaks increased as well, though POM peaks still dominate.

The bands in the FTIR spectra of the new products associated with the \([\text{SiMo}_{12}\text{O}_{40}]^{4-}\) anions are all shifted by only several inverse centimeters as compared with the pure POM. This is observed as:

- red shift of the band at 956 to 952 and 950 cm\(^{-1}\) and band 908 to 905 and 904 cm\(^{-1}\) for hybrids with POM:lignin molar ratio 1:4 and 1:16 correspondingly;
- blue shift from 859 to 867 and 870 cm\(^{-1}\) and from 778 to 798 and 797 cm\(^{-1}\) for hybrids with POM:lignin molar ratio 1:4 and 1:16 correspondingly.

This indicates [13] that the Keggin geometry of polyanions is preserved inside the lignin matrix, though being slightly distorted due to the influence of coordination with quaternized lignin cations.

The considerable shifts of bands associated with quaternized lignin, e.g. 1617 cm\(^{-1}\) in carboxyl and carbonyl groups and 1416 cm\(^{-1}\) in carboxylate ions, indicate that the lignin carbonyl groups interact as ligands with \([\text{SiMo}_{12}\text{O}_{40}]^{4-}\).

Additional structural information on the silicomolybdate portion of the lignin-[\text{SiMo}_{12}\text{O}_{40}]^{4-} was obtained by Raman spectroscopy. As shown on the figure 2, pure silicomolybdate was characterized by five bands at 660 (Mo-O\(_\text{b}-\text{Mo}\)), 800 and 880 (Mo-O\(_\text{a}-\text{Mo}\)), 920 (Mo=O), and 980 (Mo=O) cm\(^{-1}\), which is in good correlation with values found in [14]. After the interaction with quaternized lignin, apart from wide bands at 1045, 1435, 1567 cm\(^{-1}\), which belong to lignin [15], bands at 732 and 851 cm\(^{-1}\) appear, which indicates formation of complex with polyanion involvement.

![Figure 2](image_url)

**Figure 2.** Raman spectra of \(\text{H}_4\text{SiMo}_{12}\text{O}_{40}\cdot13\text{H}_2\text{O}\) (A) and the product of its interaction with quaternized lignin at co-reagents molar ratio 1:16 (B).

To obtain more detailed information about Mo valence in the hybrid materials, their EPR spectra were obtained at the temperatures in the range 10 – 293 K. No EPR signal was observed for pure \(\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]^{4+}\) in all measuring temperature range used since this compound contains Mo\(^{6+}\) ions with \(d^0\) configuration. The products of \(\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]^{4+}\) interaction with lignin at the co-reagents molecular ratios 1:4 and 1:16 exhibited at the measuring temperature of 10K a relatively isotropic signal with \(g = 1.9437\) and 1.9444, respectively, (Fig. 3 and 4), which can be attributed to Mo\(^{5+}\) (\(d^1\) configuration) [13,16]. The resonance magnetic field for this line is constant for \(T = 4 – 150\) K (figures 3 and 4).
whereas the line intensity quickly decreases (in comparison with lignin EPR line at \( g = 2.0045 \)) with increasing temperature of EPR measurement obeying a Curie law. The integral intensity of the EPR line \( \text{Mo}^{5+} \) per 1 g of the hybrid material with co-reagents molar ratio \([\text{SiMo}_{12}\text{O}_{40}]^{4-}:\text{lignin} = 1:16\) is about tenfold higher in comparison with that for \([\text{SiMo}_{12}\text{O}_{40}]^{4-}:\text{lignin} = 1:4\), confirming the partial reduction of \( \text{Mo}^{6+} \) as the result of interaction with quaternized lignin.

**Figure 3.** EPR spectra of \([\text{SiMo}_{12}\text{O}_{40}]^{4-}\) - lignin hybrid with co-reagents molar ratio 1:4 taken at temperatures: 10K (1), 60K (2), 90K (3), 120K (4) and 150K (5).

**Figure 4.** EPR spectra of \([\text{SiMo}_{12}\text{O}_{40}]^{4-}\) - lignin hybrid with co-reagents molar ratio 1:16 taken at temperatures: 10K (1), 60K (2), 120K (3) and 150K (4).

The EPR line of \( \text{Mo}^{5+} \) observed for both hybrids at 10K is narrow (\( \Delta H_{pp} \) values are 23 an 26 G for hybrid with molar ratio \([\text{SiMo}_{12}\text{O}_{40}]^{4-}:\text{lignin} = 1:4 \) and 1:16, respectively) indicates high delocalization spins of \( \text{Mo}^{5+} \) ions. With temperature increasing the line broadens and at 150K the \( \Delta H_{pp} \) values are 33 and 45 G for hybrids with molar ratio \([\text{SiMo}_{12}\text{O}_{40}]^{4-}:\text{lignin} = 1:4 \) and 1:16, respectively. The broadening of the EPR spectra with the temperature indicates that thermal electron delocalization
occurs due to paramagnetic Mo$^{5+}$ ion is surrounded by Mo$^{6+}$ ions [17] and the electron hopping occurs between metal sites. Such behavior indicates that POM portion of hybrids synthesized can be considered as mixed-valence system of class II in accordance with the Robin and Day classification with the moderate electronic interaction between the two adjacent metal centers [17].

Investigation of the nitrogen gas adsorption-desorption revealed 10 and 15 fold increases (for molar ratio silicomolybdate:lignin 1:4 and 1:16, respectively) in pore volume and surface area of hybrid materials in comparison with the parent polymer matrix. For the hybrid materials obtained at the molar ratio [SiMo$_{12}$O$_{40}$]$^{4-}$: lignin = 1:16, BET surface area was of 30 m$^2$/g, pore volume of 300 mm$^3$/g and the distribution of the pore sizes was rather narrow with the most frequently occurred pore diameter of 11 nm (about 50% of total pores area and volume), showed that the prepared materials nanoporous composites.

4. Conclusions
Nanoporous hybrid inorganic-organic material with rather narrow pore size distribution and good thermal stability was obtained via solid phase interaction of silicomolybdate heteropolyanions and plant-originated polymer lignin, varying their molecular ratio. The partly reduction of Mo (VI) to Mo (V) and complexes formation between lignin and polyoxometalate have been established by EPR, FT-IR and Raman spectroscopy. It was shown that the primary Keggin structure of heteropolyanion remains after formation of hybrid material regardless the molecular ratio of co-reagents. The EPR spectrum parameters (line width and g-value) indicate that the micro-environment of Mo ions differs in the hybrid materials obtained at the different molar ratio of [SiMo$_{12}$O$_{40}$]$^{4-}$ and lignin.

Acknowledgments
The financial supports from the EU 6th Framework Programme, Contract IRRISEASOIL, and the Latvian budget, Research grant 1564, State Programme 1-23/65 and Collaboration Programme “Integrated Utilization of Renewable Raw Materials” are gratefully acknowledged.

References
[1] Gomez-Romero P, Cuentas-Gallegos K and Lira-Canto M 2006 J. Mater. Sci. 40 1423
[2] Kim H S, Hoa D T M, Lee B-J, Park D H and Kwon Y-S 2006 Current Appl. Physics 6 601
[3] Casan-Pastor N and Gomez-Romero P 2004 Frontiers in Bioscience 9 1759
[4] Hasenknapf B 2005 Frontiers in Bioscience 10 275
[5] Han Z, Zhao Y, Peng J, Feng Y, Yin J and Liu Q 2005 Electroanalysis 17 1097
[6] Chen S-M and Fa Y-H 2004 J. Electroanal. Chem. 567 9
[7] Sequeira S, Evtuguin D and Portugal I 2007 Am. Chem. Soc. Symp. Series 954 121
[8] Telysheva G, Dizhbite T, Jashina L, Andersone A and Mironova-Ulmane N 2006 Latvian J. Phys. Tech. Sci. 2 13
[9] Feist M, Molchanov V, Kazansky L, Torchentkova E and Spitsyn B 1980 Zb. Neorg. Khym. 25 733
[10] Faix O 1991 Holzforschung 45 Suppl 21
[11] Rochiccioli C, Fourer M, Frank R and Thouvenos R 1983 Inorg. Chem. 22 207
[12] Kuzmin A, Kalendarev R, Kursitis A and Purans J 2006 Latvian J. Phys. Tech. Sci. 2 66
[13] Xu L, Wang E, Liu J and Huang R 2003 Trans. Metals Chem. 28 142
[14] Himeno S, Kitazumi I and Sano K-i 1999 Analyt. Sci. 15 35
[15] Cao Y, Shen D, Lu Y, Huang Y 2006 Annals of Botany 97 1091
[16] Niebieskikwiat D, Sanchez R D, Caneiro A, Morales L, Vasquez-Mansilla M, Rivadulla F and Hueso L E 2000 Physical Review B 26 3340
[17] Anwar M, Hogarth C A and Lott K A K 1989 J. Mater. Sci. 24 1660