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# Preparation of nanostructured porous $SiO_2$-$Al_2O_3$ oxycarbonitride materials obtained by a new chemical precursor method

**Research Article**

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**Abstract:** Nanostructured hybrid materials containing $Al_2O_3$ were synthesized *via* a sol-gel method through hydrolysis and co-condensation reactions using trimethylsilyl isocyanate (TMSI) as a new silica source in the presence of tetramethoxysilane (TMOS) and three different quantities (10, 20 and 30 wt.% ) of aluminum sec-butoxide ($Al(OBu^{sec})_3$ as a modifying agent. The xerogel nanostructured materials are pyrolyzed in nitrogen atmosphere in the temperature range from 400°C to 1100°C. The transformation of the xerogel hybrid networks into Al-Si oxycarbonitride materials has been investigated by XRD, FTIR, SEM, AFM, and $^{29}$Si MAS-NMR. To the best of our knowledge, the work reported here is the first synthesis of porous di-urethanesils modified with aluminum and one of the few examples of alumosilica oxycarbonitride materials

**Keywords:** *$SiO_2$- $Al_2O_3$ • Sol-gel method • Porous materials • Nanostructured di-urethansils • Oxycarbonitride materials*

## 1. Introduction

The chemistry of the sol-gel process based on hydroxylation and condensation of molecular precursors has been extensively studied for silica. Among porous solids, amorphous silica with large pores and broad pore size distribution, known as xerogels have a distinguished position not only at the academic level but also in practice. The scientific investigations over these materials prove that they are networks of interconnected, covalently bonded silicas or organosilicas with random distribution of pore size. Soon after this discovery, there was much interest in incorporating organic groups into the silica network in order to improve the properties of porous materials. The first idea in this direction was grafting of organic groups onto the channel walls using the reactivity of the silanol groups of the hydrolyzed tetraethylorthosilicate (TEOS), tetramethylorthosilicate (TMOS) or the organosiloxanes of the type $RSi(OEt)_3$. These modifications result in materials such as silicon carbonitride and oxycarbonitride glasses, and ceramics with useful properties.

Isocyanate-modified siloxanes are a new class of precursors containing Si-N and Si-C bonds, which are often used to obtain optical glasses by the sol-gel method, and remain stable during the synthesis process [1]. To the best of our knowledge there is not any bibliographic data for the use of isocyanate-containing alkoxides as precursors for the oxycarbide and carbonitride porous hybrid materials synthesis. In our previous study, nanostructured hybrid xerogels have been successfully prepared based on hydrolysis and condensation of tetramethylorthosilicate (TMOS) and trimethylsilyl isocyanate (TMSI) modified by titanium and zirconium. The structure and the possible mechanism of cross-linking of the hybrid gels were studied [2,3]. Trivalent metal alkoxides appear to be much more reactive than transition metal alkoxides. This is due

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to the lower electronegativity of the trivalent metals compared with silicon, and the ability of trivalent metal atoms to exhibit several coordination states [4]. Among the trivalent metal alkoxides, those of aluminum have been systematically studied both from experimental [5] and theoretical [6] points of view. There are, however, unanswered questions concerning the influence of aluminum content and pyrolysis temperature on the morphology and thermal stability of the new generation hybrid materials such as di-urethanesils.

## 2. Experimental Procedures

The organic-inorganic hybrid materials have been prepared as 80 wt.% TMOS which was dissolved in THF (in ratio 1:1) and hydrolyzed with acid water (pH=1.5) for 10 min. After that, an appropriate amount of TMSI (20 wt.%), previously dissolved in THF (1:1) was added. After 30 min of stirring at room temperature was added the necessary amount of aluminum sec-butoxide ($Al(OBu^{sec})_3$ dissolved in EtAcAc in ratio 1:1) from 10 to 30 mass.% with respect to TMOS. Mixing of the solution was continued for 40 - 60 min.

The gels were pyrolyzed up to 1100°C for 90 minutes in nitrogen atmosphere with a heating rate of 10°C $min^{-1}$. All materials were studied using XRD (Rigatcu 30 mA, 40V, scan speed 3° 20/min in Debye-Scherrer geometry), FTIR (Mattson 7000), NMR ($^{29}Si$ solid state NMR spectra were recorded at 79.79 MHz on a Bruker Avance 400 spectrometer, measured with 40° pulses) AFM (NanoScope Tapping ModeTM), and SEM (Hitache S4000 Field Emission) investigation.

## 3. Results and Discussion

The data obtained from XRD study of the hybrid xerogels and the samples pyrolyzed up to 1100°C proved that all materials have an amorphous structure (Fig. 1a and b). The XRD spectra show a broad peak at $2\theta = 24^o$, considered to arise from the inorganic part of the hybrid materials. From the bibliographic data [7], this peak is connected with amorphous $SiO_2$ and remains constant, irrespectively of aluminum concentration.

Fig. 2a presents the FTIR spectra of the samples containing 10 and 30 wt.% Al at room temperature and after pyrolysis at 800 and 1100°C. It is interesting to note that the bands observed in the frequency range from 1600 to 1750 $cm^{-1}$ correspond to the vibrations of the urea- and urethane- bonds which are formed during the polycondensation processes. The bands detected at 1746 $cm^{-1}$ are due to the C=O vibration and those at 1707 $cm^{-1}$ can be explained by the presence of NH-CO-O groups. The contribution of NH-CO and CO-NH bonds results in bands visible at 1660 $cm^{-1}$ and 1632 $cm^{-1}$, respectively. The vibrations of the $Si-NH_2$ groups can be observed as a band at 1210-1230 $cm^{-1}$ [8]. The peaks at 1080 $cm^{-1}$ and 480 $cm^{-1}$ are due to both stretching and deformation vibration of Si-O-Si bonds, while the deformation vibration corresponding to $Si-(CH)_3$ groups has appeared at 845 $cm^{-1}$ and 765 $cm^{-1}$ [9].

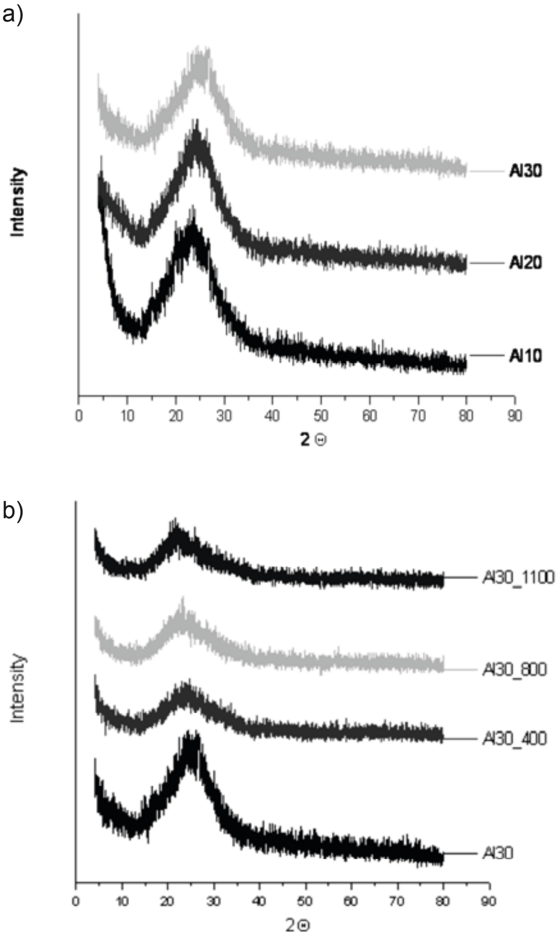

**Figure 1.** XRD investigation of xerogels containing different Al content (a) and xerogel containing 30 wt.% Al pyrolyzed up to 1100°C (b).

Evidence for the chemical homogeneity of the hybrid materials can be considered from the presence of peaks at 648 $cm^{-1}$, which in the bibliographic data is referred to the presence of heterometallic (Si-OAl( Si) bonds, as well as the linkages at 547 $cm^{-1}$ due to deformation vibration of O-Si (Al)-O). According to these results the hybrid structure is built from $SiO_2$-$AlO_6$ polyhedra and $Si-CH_3$ repeating structural units, grafted onto siloxane network by urethane (-NHC(=O)-) bridges in the presence of ureasil monomers [10]. Therefore the organic and the inorganic parts in the gels are linked to each other *via* covalent bonds and form a single homogeneous phase. According to [11] such hybrid materials are accepted as nanostructural materials.

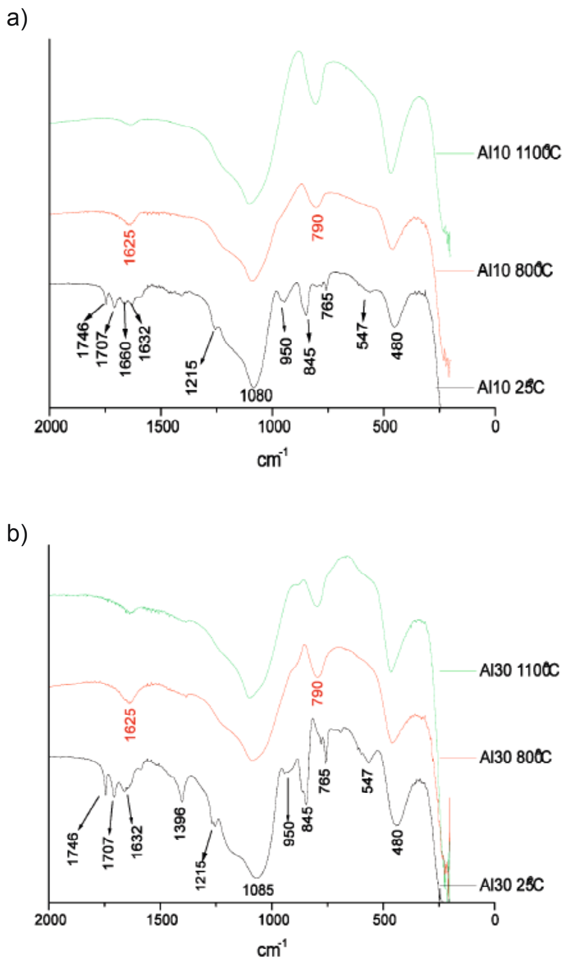

**Figure 2.** FTIR spectra of xerogels containing different Al content (a) and xerogel containing 30 wt.% Al pyrolyzed up to 1100°C (b)

The obtained hybrid xerogels undergo two structural changes during pyrolysis at 800°C (Fig. 2b). The bands visible in the range 1600 $cm^{-1}$ - 1750 $cm^{-1}$ are transformed into a common peak at 1670 $cm^{-1}$ which is associated with the vibrations of N-C-N groups. The second change refers to the vibrations of $Si-CH_3$ (845 $cm^{-1}$ and 765 $m^{-1}$) and Si-O-Si (804 $cm^{-1}$) groups. After pyrolysis these peaks are converted into one common band at 790 $cm^{-1}$. According to many authors [7] this change is due to the transition of a hybrid organic-inorganic network to an oxycarbide amorphous material and in this case in the presence of nitrogen and aluminum. Consequently, the hybrid structure retains stability up to 800°C, and at this temperature the pyrolyzed nanostructured materials can be explained as Si-Al oxycarbonitride amorphous materials, stable up to 1100°C.

The obtained $^{29}Si$ CP MAS NMR spectrum confirms the FTIR investigations and proves that Al, C and N are present in the building of the siloxane network. The $^{29}Si$ MAS NMR spectrum for the gel with maximum aluminum content (30 wt.%) is shown on Fig. 3. The observed resonances centered at -110 and -96 ppm are due to $Q^4$ ($Si(OSi_4)$) and $Q^3$ ($AlSiO_3$) structural units respectively [12]. The half-line at -91 ppm has been related to the $Q^2$ structural units of the silicon, namely $Si(OSi)_2(OH)_2$ [10]. Moreover, in the NMR spectrum the resonance centered at +14 ppm due to $M\ (CH_3)_3SiNH$ structural units is observed. Therefore by use of TMSI as precursor, Si-N and Si-C bonds remain stable after hydrolysis-condensation processes.

In order to illustrate the Al content, the structure of the derived amorphous materials was characterized using $^{27}Al$ solid-state NMR. Fig. 4 presents the NMR spectrum of the gel modified with 30 wt.% Al. Six-fold coordinated aluminum spaces observed in the IR spectra are established by the $^{27}Al$ NMR signal at $\delta = 0$ ppm.

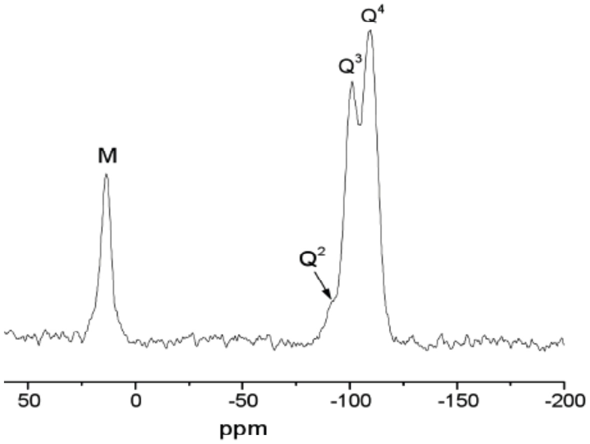

**Figure 3.** $^{29}Si$-MAS NMR of gel modified by 30 wt.% Al

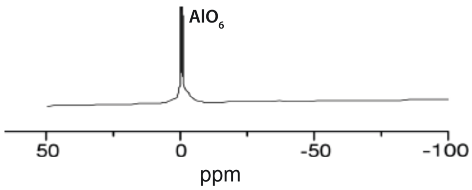

**Figure 4.** $^{27}Al$-MAS NMR of gel modified by 30 wt.% Al

This coordination state is formed when the alkoxides such as $Al(OR)_3$ was used even when $Si(OR)_4$ is prehydrolysed before mixing with $Al(OR)_3$. The tetracoordinated aluminum atoms can be obtained after pyrolysis up to 600°C.

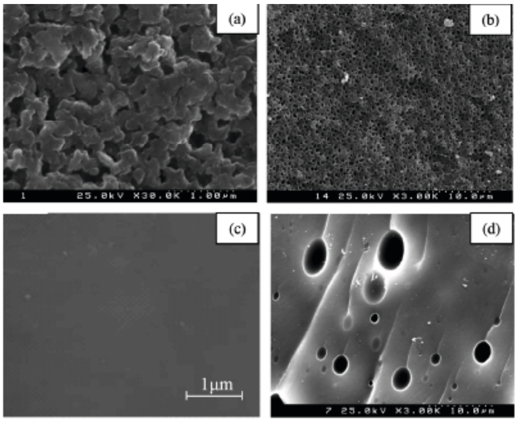

**Figure 5.** SEM images of samples with 10wt.% Al at room temperature (a); 10 wt.% Al pyrolyzed at 1100°C (b); 30 wt.% Al at room temperature (c) and 10 wt.% Al at 1100°C (d)

The pore morphology formation in the $SiO_2$-$Al_2O_3$ hybrid materials was well interpreted by means of SEM and AFM investigations. From the SEM study (Fig. 5) it was observed that the xerogel with 10 wt.% Al content, (Fig. 5a) possesses the highest degree of open porosity with a characteristic pore size of 240 nm. This porous structure is retained after pyrolysis up to 1100°C (Fig. 5b) but the pore size is increased up to 600 nm, which results from combustion and evaporation of organic components from the bulk of the materials. The cross-section surface of this sample was investigated by means of an AFM study in order to determine if the pores in the materials were linked to each other (Fig. 6). It was observed that at low Al content (10 wt.%) the xerogels are characterized by a canal structure as a result of pores being linked to each other and uniformly distributed in the bulk of the sample (Fig. 6a). The RMS (Root Mean Square) surface roughness was defined, and it is of the order of 7 nm for the xerogel (Fig. 5a) and increased up to 46 nm for the pyrolyzed sample (Fig. 6b). The SEM (Fig. 5c) and AFM (Fig. 6c) images of a xerogel with higher Al content (30 wt.%) show a smooth and vitreous surface with the RMS roughness around 0.3 nm. After thermal treatment at 1100°C, it was observed that pores had appeared and their size calculated to be between 1 and 3 µm (Fig. 5d). Furthermore, the presence of a crystalline-like object with a preferred orientation is observed for this composition in the SEM image. This behavior was supported in the AFM image which is presented on Fig. 6c. The RMS roughness of the surface of the samples at this temperature (1100°C) is increased up to 14 nm as a result of the appearance of crystals at the nanometer scale.

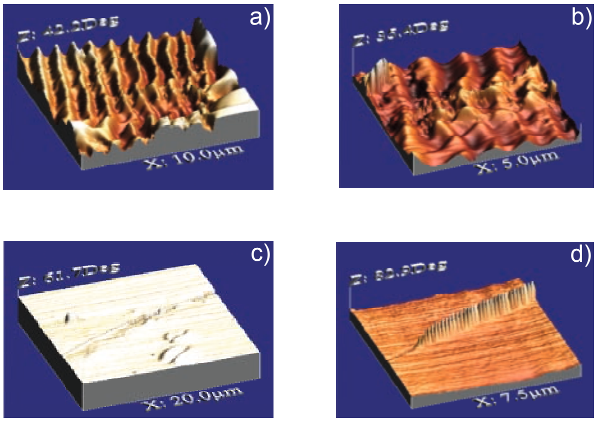

**Figure 6.** AFM images of samples with 10 wt.% Al at room temperature (a); 10 wt.% Al pyrolyzed at 1100°C (b); 30 wt.% Al at room temperature (c) and 10 wt.% Al at 1100°C (d)

## 4. Conclusion

Novel di-urethanesil hybrid materials modified by aluminum were successfully prepared for the first time via a new chemical precursor method using tetraethylorthosilicate, trimethylsilyl isocyanate and aluminum sec-butoxide. From the XRD, FTIR and NMR results, the structure of the derived xerogels can be described as amorphous porous materials built from Si-O-Al and $Si-CH_3$ repeated structural units covalently bonded onto the siloxane network by urethane (-NHC(=O)-) bridges to form a di-urethanesil backbone. After pyrolysis at 800°C the hybrid structure is transformed into a Si-Al oxycarbonitride material built from Si-O-Al, Si-O-Si, Si-C and Si-N bonds. The pore morphology formation in the obtained materials was well interpreted by means of AFM and SEM investigations. According to these results, the pores are linked to each other and their size can be successfully controlled by the pyrolysis temperature and the $Al_2O_3$ concentration. The relationship between the hybrid material structure and the future properties of the derived new sol-gel products will be the subject of our next work.

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