

- one dimensional photonic energy transfer to funnel the electronic excitation along the nanochannel of the inclusion compound [14,25]
- macroscopic NLO response exploiting the head-to-tail arrangements of suitable push-pull molecules within the channel.

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## Effect of anilines as a synthesis component on the hydrophobicity of silica

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### 1. INTRODUCTION

In the field of polymeric systems an important goal is to reinforce the polymer matrix and to improve mechanical and thermal properties. Inorganic additives are introduced into polymer systems as fillers or as reinforcing agents. Among the hybrid organic-inorganic powdered materials, the silica receives considerable interest because different degrees of hydrophobic/hydrophilic are determining its dispersion in the polymeric matrix. The synthesis and characterization of hybrid organic-inorganic powdered materials have received great attention in past years. These materials present properties related to the matrix as well as the organic phase, which can be combined in order to obtain new materials. The sol-gel method is an important route to prepare such materials using alkoxysilanes R-Si(OR)<sub>3</sub> and tetraethylorthosilicate (TEOS) as precursors. The polycondensation of alkoxysilanes can be described in three steps: (i) hydrolysis, (ii) silanol condensation and (iii) silanol-alcohol condensation.

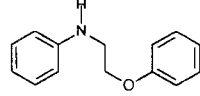
The relative simplicity and versatility of the sol-gel process, when compared to covalent-bonding methods to obtain hybrid materials, associated with low cost, are responsible for its extensive utilization. The possibility of obtaining different physicochemical characteristics like surface area, particle shape and size, porosity and organic functionalization grade, are some advantages of this process [1-3]. However, a little change in the parameter conditions of the synthesis, like solvent, catalyst or silane amount, can produce great modifications in the final properties of the materials. In this context, the study of the synthesis conditions and the related resulting properties are very important to understand these systems [4].

The silica can have hydrophobic properties when its surface is functionalized. This process requires the presence of silanol groups at the surface. There are many types of silica differing in their surface properties, in particular, the density of silanol groups and the types of silanols (isolated, hydrogen bonded, geminal) vary by techniques of preparation of silica. The purpose of this investigation is to know the grafting process on silica prepared by sol-gel. The principle of the investigation work consists in comparing the grafting of anilines, with different active groups, on silica to obtain different degree of the surface hydrophobicity. For a better understanding of these solids, the characterization of the nature of the species was determined by FT-IR, XRD, DTA-TGA and surface area (S<sub>BET</sub>).

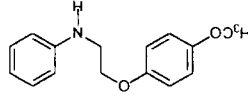
## 2. EXPERIMENTAL

### 2.1. Silica preparation by sol-gel technique

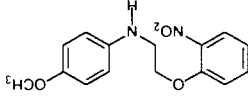
All the experiences were made with final molar ratio of TEOS/EtOH/H<sub>2</sub>O equal to 1:1:4. The TEOS-EtOH-AcH sols were stirred at atmospheric pressure at room temperature (r.t.), during 30 min. Then, the hydrolysis process began with slow addition of distilled water. After the water addition, gelation of the sols was carried out at r.t. and the wet gels were then aged in the same medium until dry silica particles were obtained. These solids were washed with ethanol and distilled water. After that, they were dried at r.t. and calcined to 673, 873 and 1073 K.



- *N*-(2-phenoxyethyl)aniline is named **A42**



- *N*-(2-(4-methoxyphenoxy)ethyl)aniline is named **A45**



- *N*-(2-(2-nitrophenoxyethyl)aniline is named **A57**

### 2.2. Functionalization of silicas

The (grafting agents) were anilines. prepared in our laboratory [5] (Scheme 1). The functionalized silica was prepared by addition of aniline to a suspension of silica in refluxing toluene, stirred for 5 h. The solid was filtered, washed in a Soxhlet apparatus with diethylether and dichloromethane and then dried, at 393 K [6].

### 2.3. Characterization

*Textural properties.* N<sub>2</sub> adsorption and desorption isotherms at 77 K were carried out using a Micromeritics Accusorb 2100 equipment. *FTIR.* A Bruker IFS 66 equipment, pellets in Brk and a measuring range of 400-4000 cm<sup>-1</sup> were used to obtain the FT-IR spectra of solids. *X-ray diffraction.* The XRD patterns were obtained by using a Philips PW-1714 diffractometer with built-in recorder.

## 3. RESULTS AND DISCUSSION

Sol-gel technology is a widely researched field and the hybrid organic-inorganic materials can be fabricated by carrying out the inorganic sol-gel process in presence of organic species, which are capable of interacting chemically with the metal alkoxides. "Hybrid material" means a disordered physico-chemical system that forms intricate organic and inorganic networks [7]. The degree of linking and cross-linking of the organic and inorganic networks influences the mechanical and chemical properties and can be controlled by varying, for example, the catalyst used [8]. In this work, the acetic acid was used and the influence of stirring was reported in previous paper [9].

Table 1 shows the specific surface areas (S<sub>BET</sub>) of the samples as a function of heat treatment procedures employed. These results show a decrease of S<sub>BET</sub> for an increase of the FTIR spectroscopy has been used to study the structure of the silica and hybrid material.

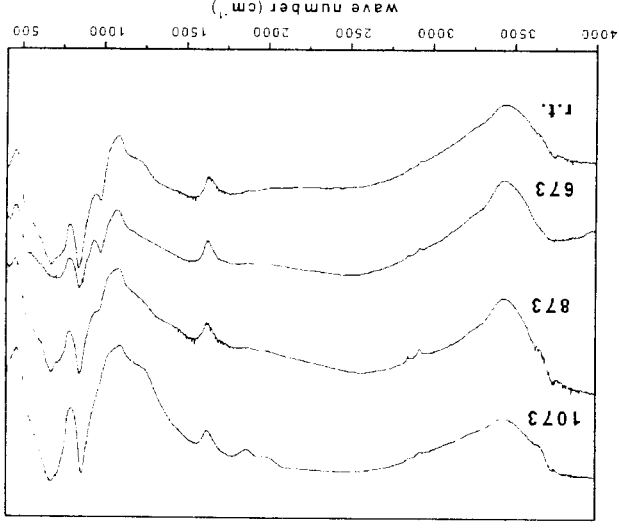


Fig. 1. FTIR spectra of silica, obtained by sol-gel, at different temperatures.

S <sub>BET</sub> (m <sup>2</sup> /g)	r.t.	673	873	1073
	431	312	131	0.6

Table 1. S<sub>BET</sub> of silica, obtained by sol-gel, at different temperatures

Figure 1 shows the spectra of the silica prepared by sol-gel at r.t. and calcined to 673, 873 and 1073 K, respectively. For silica, the broad adsorption positioned in the range 3000-3800 cm<sup>-1</sup> is due to H-bonded silanols. In addition, this band is attributed to the presence of hydroxyl groups of water present on the surface, at r.t. Additionally, bands corresponding to Si-O-Si symmetric and asymmetric vibrations are located at 812 and 1104 cm<sup>-1</sup>, respectively. The small shoulder at 959 cm<sup>-1</sup> can be assigned to the Si-OH group. During the heat treatment investigations have correlated the surface dehydroxylation with two bands at 490 cm<sup>-1</sup> (called D) and 604 cm<sup>-1</sup> (D<sub>2</sub>) that are superimposed on the broad band at about 440 cm<sup>-1</sup>, which is the most intense signal in the spectrum of v-SiO<sub>2</sub> [10].

In this research, representative substituted *N*-phenoxyethylanilines were used as functionalizing: *N*-(2-phenoxyethyl)aniline (**A42**), *N*-(2-(4-methoxyphenoxy)ethyl)aniline (**A45**) and *N*-(2-(2-nitrophenoxyethyl)aniline (**A57**), respectively. The pK<sub>a</sub> for all anilines are showed in Table 2. The acid dissociation constants of the *N*-phenoxyethylammonium ions were attained by fluorescence spectrometry [11]. The results showed that, when there is a *p*-methoxy group at the *N*-phenyl ring (**A45**), the acidity of the aryl alkyl ammonium ion is

lowered compared to the unsubstituted compound (A42). The OMe group may produce a decrease electron density at the N atom through proton chelation. The lowering acidity effect increases when the methoxy group changes its position and there is a nitro group in its place (A57).

Table 2. pKa of anilines

Aniline	R	R'	pKa
A42	H	H	3.83
A45	H	OMe	3.70
A57	OMe	NO <sub>2</sub>	3.40

The immobilization of the aniline groups on the matrix surface silica was studied by FTIR. Spectra of silica and functionalized silica with A42, A45 and A57 anilines, at r.t. and 393 K are presented in Figure 2.

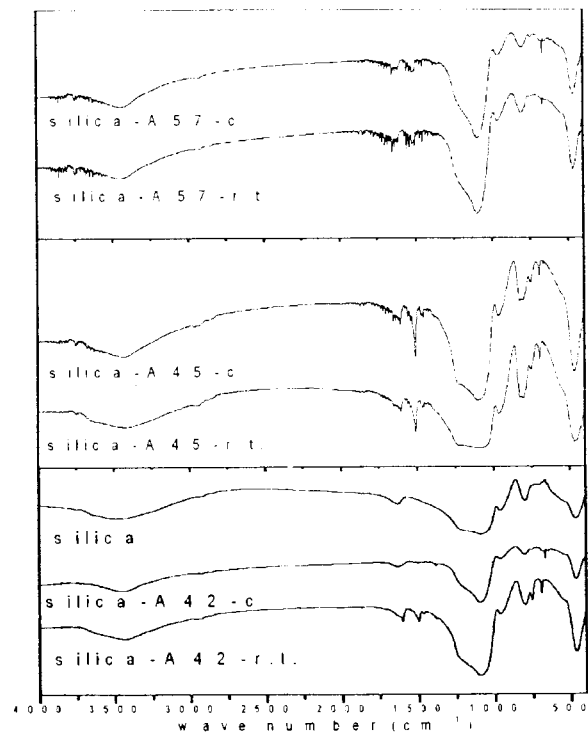


Fig. 2. FTIR spectra of functionalized silica with anilines, at room temperature (r.t.) and calcined at 393 K (c).

The main differences between functionalized silica spectra and that of the pure silica are due to: the N-H stretching band (3300-2600 cm<sup>-1</sup>, broad peak, overlapped with the stretching bands of silanol of silica and -CH<sub>2</sub>- groups), overtone band (1975 cm<sup>-1</sup>). Two possible vibrational bands: asymmetrical -NH<sub>3</sub><sup>+</sup> bending band (1600 cm<sup>-1</sup>) and the symmetrical -NH<sub>3</sub><sup>+</sup> bending band (1500 cm<sup>-1</sup>) [12].

As the occurrence of reactions involving amino groups, with the consequent formation of new species, is unlikely, these additional components could be assigned to amino-ethyl species experiencing some peculiar interaction with the boundary. The complexity of bands due to such species indicate the presence of some heterogeneity, this behaviour could be due to constraints of amino-ethyl species in the silica gel framework [13].

The mode of anchorage of the organic compounds is of prime importance for the characteristics of the final functionalized silica. After functionalization, it was determined the degree of hydrophobicity of silica surface, with water (H<sub>water</sub>) and wettability, with ethanol (M<sub>Ethanol</sub>), respectively. Table 3 shows these properties for silica synthesized by sol-gel and functionalized with A42, A45 and A57 anilines, at r.t. and calcined (c). In according to functional groups of anilines, the hydrophobicity degree is very good for silica-A42-c but is it inexistent for silica-A57-r.t., respectively. In relation to ethanol wettability, the functionalized silica presents a different behavior that could be due to particular interaction of the surface sites with water than with ethanol molecules.

Table 3. Hydrofobicity degree (H<sub>water</sub>) and Ethanol wettability (M<sub>Ethanol</sub>)

	H <sub>water</sub>	M <sub>Ethanol</sub>
Silica	0	1
Silica A42-r.t	0.64	0.42
Silica A42-c	0.88	0.21
Silica A45-r.t	0.16	1.21
Silica A45-c	0.43	1.42
Silica A57-r.t	-0.54	2.00
Silica A57-c	0.31	1.21

In addition these results evidence the preservation of hydrophilic patches on the silica surface. This hypothesis has been taken into account during the functionalization procedure in solvent as toluene, perhaps in polar solvents and different treatments of silica surface this behavior is made by other alternative routes.

The final mechanism for our systems is in study and these results will be analyzed according to different possible mechanisms in order to discriminate between them.

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## Removal of cadmium, zinc, copper and lead by red mud, an iron oxides containing hydrometallurgical waste

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Red mud, a residue of the alumina production industry which is actually a solid waste, has been studied as a potential sorbent for the removal of toxic bivalent cations (i.e. Cd, Zn, Cu and Pb) from aqueous solutions in the presence of 0.01 M NaNO<sub>3</sub>. The experimental data were modeled with Langmuir and Freundlich isotherms and fitted quite well. The relatively high uptake indicated that red mud can adsorb considerable amounts of cadmium and zinc from near-neutral aqueous solutions (maximum uptake capacity for cadmium: 68 mg·g<sup>-1</sup> at pH 6 and ca. 133 mg·g<sup>-1</sup> for zinc at pH 7). A significant uptake was also observed for copper and lead at pH 6 and 7 respectively which was attributed to precipitation of the respective insoluble hydroxides. TCLP leaching tests before and after the metal removal have shown that red mud is an environmentally compatible material that could be used for the wastewater treatment. Regeneration possibilities have also been observed.

### 1. INTRODUCTION

The presence of heavy metal ions in the environment is of major concern due to their toxicity to many life forms. Unlike the organic pollutants, metal ions do not degrade into harmless end-products. The increasingly stringent European legislation on the purity of drinking waters and on the concentration of contaminants in wastewaters has created a growing interest in the development of treatment processes for the removal of hazardous metals from aqueous solutions. Among the various methods proposed for this purpose adsorption proved to be of the most promising ones [1, 2]. Several natural (e.g. natural zeolites, bentonites, metal oxides) and synthetic (e.g. synthetic zeolites, resins, metal phosphates and silicates, synthetic oxides/hydroxides/hydroxyoxides) materials have been investigated as sorbents for heavy metal removal from solutions achieving different levels of success [3, 4–9]. Moreover, considerable research work has been done on various industrial waste materials in order to develop suitable sorbents for water treatment; so fly ash [10, 11], blast furnace slug [12], biomass [13, 14] and bagasse fly ash [15], among others have been tested as sorbents for heavy metal removal with various levels of success.

The aim of this work was to investigate the possibility to use red mud for the water and wastewater treatment. Red mud is an insoluble fine-grained residue of alumina production industry (Bayer process: extraction of alumina from bauxite by treatment of the ground ore with hot concentrated base) [16, 17]. The major constituents of red mud are Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, SiO<sub>2</sub> and Na<sub>2</sub>O [e.g. 18–20]. Since ca. 1.0–1.5 tones of red mud are produced for