SILICE NANOSTRUCTURATĂ DOPATĂ CU Cr OBŢINUTĂ PRIN INTERMEDIUL AGENŢILOR DE DIRECŢIONARE A STRUCTURII ŞI A TRICARBONIL-CROM-1-FENILETILAMINEI CHORALE
Cr- DOPED NANOSTRUCTURED SILICA OBTAINED *VIA* STRUCTURE DIRECTING AGENTS AND CHIRAL 1-PHENYLETHYLAMINE-TRICARBONYL-CHROMIUM

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Raportăm sinteza unor silice dopate cu Cr cu diferite morfologii obţinute prin polimerizarea sol-gel a tetraetoxisilicatului în prezenţa unor organogelifianţi derivaţi de D-sorbitol (1,3 :2,4-bis-O-benzilidene-D-sorbitol, DBS şi derivaţii săi substituiţi cu grupe nitro şi metoxi) şi a bromurii de hexadeciltrimetilamoniu, catalizată de S-(+)-1-feniletilamină-tricarbonil-crom care este şi sursa de Cr pentru o încărcare de 10% Cr/SiO_2. Au fost observate două tipuri de morfologii : tuburi de silice cu diametre de 300-500nm şi lungimi între 10-15µm pentru organogelifiantul cu grupe nitro şi respectiv granule aglomerate tip « colier » pentru ceilalţi Analizele EDX şi XPS au arătat o distribuţie uniformă a ionilor de Cr pe suprafaţa matricei de silice constând în 80%Cr^{3+} şi respectiv 20%Cr^{6+} .

We report the synthesis of Cr-doped silica with different morphologies by sol-gel polymerization of tetraethoxysilicate in the presence of D-sorbitol derived organogelators (1,3:2,4-bis-O-benzylidene-D-sorbitol, DBS and its p-nitro and p-methoxy derivatives) and hexadecyltrimethylamonium bromide with S-(+)-1-phenylethylamine-tricarbonyl-chromium, acting both as chiral catalyst and source of chromium, for a 10 wt% Cr/SiO_2 loading. Two different types of morphologies were observed: silica tubes with 300-500nm diameter and 10-15µm length for the nitro-substituted template and "necklace" type agglomerated silica granules for the other templates. EDX and XPS analyses revealed a uniform distribution of Cr ions on silica matrix consisting of 80% Cr^{3+} and 20% Cr^{6+}.

Keywords: *sol-gel, Cr-doped nanostructured silica, arene-tricarbonyl-chromium complexes, organogelator*

1. Introduction

Chromium ions incorporated in silica matrices with different morphologies are of great interests for spectroscopy and laser physics [1-4], anticorrosion pretreatments of metal substrates [5] and catalysis. Morphologies of the silica matrices, the nature of Cr ions and the chromium content (% wt Cr/SiO_2), affords special catalytic properties. Such catalysts are extensively utilized for ethylene polymerization [6], and scarcely in dehydrogenation [7, 8,] and oxidation reactions [9]. Several methods are reported for the preparation chromium doped silica, chemical vapor deposition [10], sol-gel technique [5, 11-14] and treatment of preformed silica matrices with organometallic compounds [15, 16].

The sol gel polymerization of tetraethoxysilicate (**TEOS**) and its derivatives is a relatively low temperature procedure which allows the control of morphology of the nanostructured silica by using different structure directing agents (**SDA**) and the incorporation of a large number of organic and inorganic additives [17-19]. The use of organogelators as templates for nanostructured inorganic and hybrid materials, first reported more

than ten years ago [20], was summarized and discussed in a recent review [21]. Applications of sol-gel technology in order to obtained doped silica matrices present a common problem: attainment of a uniform distribution of doping constituents in the matrix. In the stage of wet gels, metallic ions migrate freely in the matrix and have the tendency to aggregate in clusters at the surface of the material during thermal treatment of the gels.

In this paper we report the synthesis of nanostructured chromium-doped silica with different morphologies by sol-gel polymerization of tetraehoxysilicate (**TEOS)** in the presence of mixtures structure directing agents (**SDA**), D-sorbitol derived organogelators, (1,3:2,4-bis-*O*-benzylidene-D-sorbitol, **DBS** and its *p*-nitro, **p-NO₂-DBS** and *p*-methoxy, **p-CH₃O-DBS**, derivatives, previously synthesized [22-23]) and an ionic surfactant, hexadecyltrimethyl ammonium bromide (**CTAB**), with S-(+)-1-phenylethylamine-tricarbonyl-chromium, (**MBA-Cr(CO)₃**) acting both as a chiral catalyst and a source of chromium.

We used the *in-situ* co-assembly templating strategy [21] in order to achieve an intimate contact of the catalyst/source of chromium with the template

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self-organized as nanofibrils and **TEOS**, thus preventing the migration of the doping agent in the formed silica matrix (Figure 1). The additional **SDA**, the ionic surfactant **CTAB** facilitates the contact between reagents and template and improves the transcription process [24].

2. Experimental

Equipment

• ^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer. Approximately 0.2 M (for ^{1}H-NMR spectra) solution in CDCl$_3$ and TMS as internal standard were used. Reported data refer to chemical shifts (ppm, TMS), multiplicity, intensity of the signal and attribution.

• IR spectra were recorded on FTIR Bruker Equinox 55 equipment in KBr.

• Optical rotation was measured with Jasco P-2000 polarimeter.

• SEM analyses were performed on a HITACHI S2600N scanning electron microscope with EDX, in primary electrons fascicle, on samples covered with a thin silver layer.

• X-Ray Photoelectron Spectra were recorded on Thermo Scientific KAlpha equipment, fully integrated, with an aluminum anode monochromatic source. Survey scans (0-1200 eV) were performed to identify constitutive elements.

Sol-gel polymerization of TEOS

In a typical experiment, 30 mg (1 equiv) of organogelator and 5-7 mg (0.25 equiv.) **CTAB**, were dissolved in 3mL absolute ethanol with heating and occasionally stirring. To the clear solution 40 mg (2 equiv.) of **MBA-Cr(CO)$_3$** were added and the mixture was omogenized for 5 min. using vibrations. To the yellow viscous solution 0.27 mL (16 equiv) **TEOS** partially hydrolized by previous stirring for 15 min with 0.1 mL (7,5 equiv) water were added and the stirring was continued for 5 min. The sample was sealed in a glass tube and left for maturation for 7 days (~170 hrs.). Subsequently the sample was heated at 100°C for.

6 hrs, then at 200∘C for 2 h, under vacuum (~10 mm Hg). The solid residue was then calcinated for 6 hrs at 650°C under atmospheric conditions

S-(+)-1-phenylethylamine-tricarbonyl-chromium, **MBA-Cr(CO)$_3$** was prepared in 70 % yield by direct complexation of the S-(-)-1-phenylethylamine with Cr(CO)$_6$. From 0.6g (5 mmoles) and 1.1 g (5 mmoles) Cr(CO)$_6$ in 12mL diglyme:n-heptan 1:5, 4 hrs. at reflux (160°C) under argon, after solvent removal and separation by column chromatography (Al$_2$O$_3$, ether), **MBA-Cr(CO)$_3$** was obtained a yellow oil (0.82g, 3.5 mmoles) $[\alpha]_D^{20}$ = + 89° (c= 0.65, CHCl$_3$, e.e 98%).

^{1}*H-NMR* (δ, CDCl$_3$, TMS): 1.37, d, 3H (J= 6.5Hz, CH$_3$); 3.85, q, 1H (J=6.2Hz, CH); 5.64, d, 1H (H^2)5.29-5.41, m, 4H, (H^3- H^6).

^{13}*C-RMN* (δ, CDCl$_3$, TMS): 26.3 (CH$_3$); 50.0 (CH$^\alpha$); 90.4, 92.4, 93.1, 92.5, 93.3, (C^2-C^6); 119.4 (C^1); 233.5 (Cr-CO).

IR (cm^{-1}, neat): 3100-3500 (ν_{N-H}); 3088.7 (ν_{Car-H}); 2971.7 and 2928.5, (ν_{Csat-H}, assym); 2870.3 (ν_{Csat-H}, sym); 1964.6 and 1866.8 (($\nu_{C\equiv O}$, Cr-CO); 1594.6 (δ_{N-H}).

3. Results and discussion

The templated sol-gel synthesis of nanostructured silica above the isoelectric point of the silica precursors (pH>2) mediated by an organogelator as **SDA** requires a strong interaction between the anionic silicate and the template [25]. As a consequence, a large majority of the successfully employed compounds in transcription are cationic or neutral and contain amino functional groups. This structural requirement may be surpassed by the use of benzylamine [26] as a catalyst which interacts with the organogelator nanofibrils through π-π stacking (Figure 1). We have recently reported [27] our attempts to prepare nanostructured silica mediated by nitrogen containing **DBS** derivatives in the presence of benzylamine.
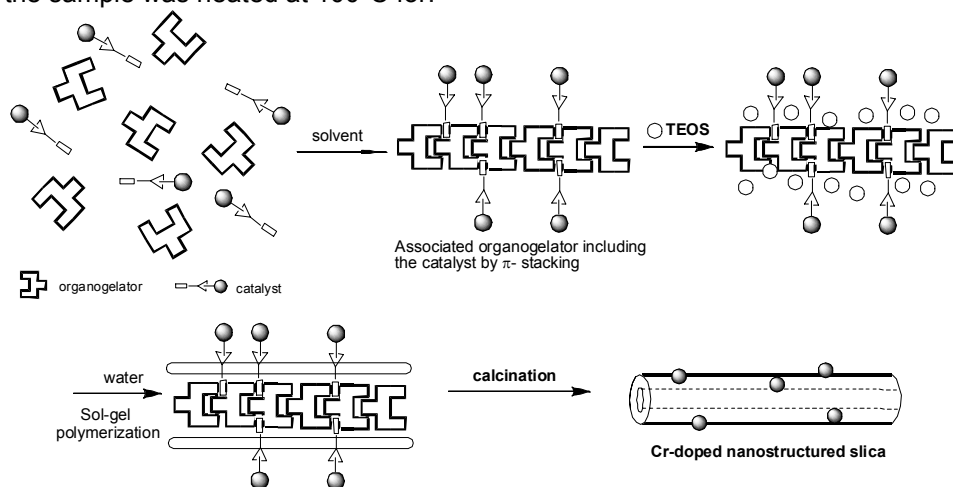

Fig. 1 – Templating strategy, *in-situ* cossembly, used for the preparation of Cr-doped silica/ *Stategia de sinteză, co-asamblare in situ, utilizată pentru prepararea silicei dopate cu Cr.*

In this paper for sol-gel polymerization of **TEOS** we utilized as **SDA**, mixtures of **DBS** or its substituted derivatives with **CTAB**. We have replaced the benzylamine with S-(+)-1-phenylethylamine-tricarbonyl-chromium in order to prepare Cr-doped silica with an even distribution of the ion metals in the silica matrix due to the association of the catalyst with the template prior to sol-gel polymerization, phenomenon that we supposed to prevent the migration of the Cr atoms in the wet gel state. Although the chiral morphology of an organogelator may be efficiently transcribed into silica [21], there are no reports of the use of a chiral catalyst to lead to the same result.

The morphology and Cr distribution of the synthesized Cr-doped silica samples was investigated by scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDX). Different morphologies were observed in close relation with the morphologies of the xerogels obtained from the corresponding organogelator in different solvents [22, 23] and. The results are summarized in Table 1 and Figure 2 and 3.

Thus, for **p-NO$_2$-DBS** template, hollow silica tubes with 300-500 nm in diameter and 10-15 μm in length were observed (Figure 2b) while **DBS** and methoxy-substituted **p-CH$_3$O-DBS**, lead to the formation of "necklace" type agglomerated silica granules with ~200 nm diameter. Taking into account the morphology of the xerogels formed by the corresponding templates, **DBS** derivatives **p-NO$_2$-DBS,** well-defined fibrils with 200-300 nm diameter (Fig. 3a, [22]) and tightly-packed fibrils as ropes for **p-CH$_3$O-DBS**, respectively (Fig. 3b, [23]) we may conclude that the transcription process mediated by the organogelators and cationic surfactant **CTAB** consist of two paralel mechanism: formation of the siloxane granules mediated by **CTAB** and aglomeration of the formed granules at the surface of the organogelator fibril. A well-definite fiber facilites the transcription process leading after maturation and thermal treatment to the formation of hollow tubes while closely-packed fibers determine only a primary organization, "necklace" type.
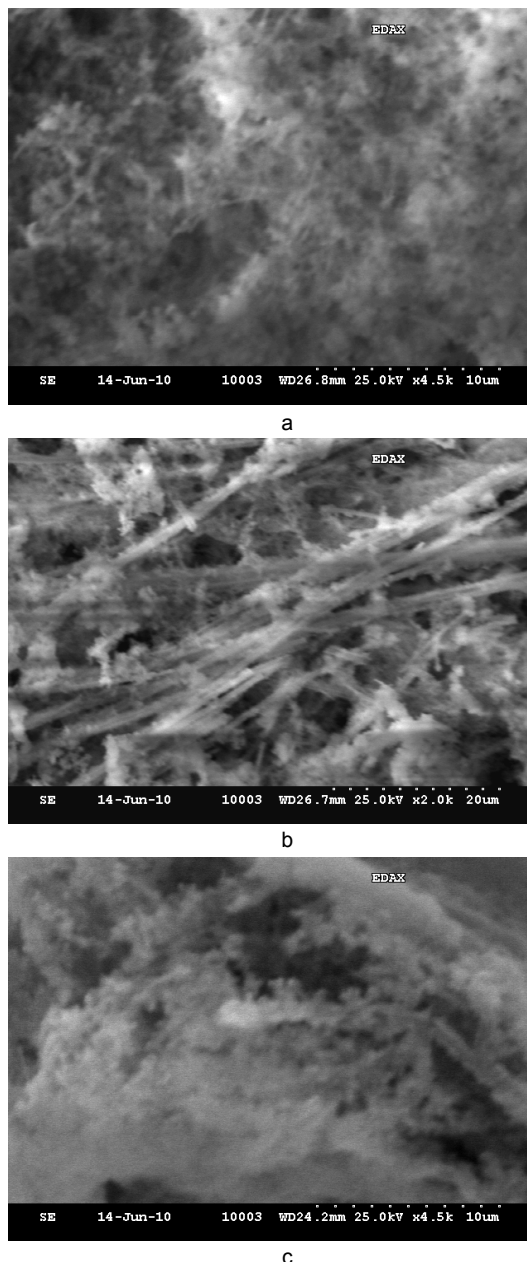
a

b

c

Fig. 2 - Morphologies for Cr-doped silica obtained by sol-polymerization of **TEOS** in the presence of mixtures of **SDA**/ *Morfologia silicei dopate cu Cr obţinute prin polimerizarea TEOS în prezenţa de amestec de SDA:* a) **DBS/CTAB/MBA-Cr(CO)$_3$**; (b) **p-NO$_2$ -DBS/CTAB/ MBA-Cr(CO)$_3$**; (c) **p-CH$_3$O-DBS/CTAB/ MBA-Cr(CO)$_3$**

Table 1

Sol-gel polymerization of **TEOS** with mixtures of **SDA** (organogelator +**CTAB**) and **MBA-Cr(CO)$_3$** catalyst
Polimerizare sol-gel a TEOS cu amestec de SDA (organogelifiant+ CTAB) şi catalizator MBA-Cr(CO)$_3$

Ent.	Organogelator *Organogelifiant* 1g/100mL	Solvent *Solvent*	Surfactant *Tensioactiv*	Reaction time/ *Timp de reacţie*	Catalyst *Catalizator*	Silica Morphology *Morfologie silice*
1.	**DBS**	ethanol	**CTAB**	170	**MBA-Cr(CO)$_3$**	Agglomerated "necklace" granules *Granule agglomerate tip "colier"* 200nm in diameter, *(Fig 2a)*
2.	**p-NO$_2$ -DBS**	ethanol	**CTAB**	170	**MBA-Cr(CO)$_3$**	Hollow tubes/ *Tuburi goale* 500-1000nm in diameter, *(Fig 2b)*
3.	**p-CH$_3$O -DBS**	ethanol	**CTAB**	170	**MBA-Cr(CO)$_3$**	Agglomerated "necklace" granules *Granule agglomerate tip "colier"* 200nm in diameter, *(Fig 2c)*

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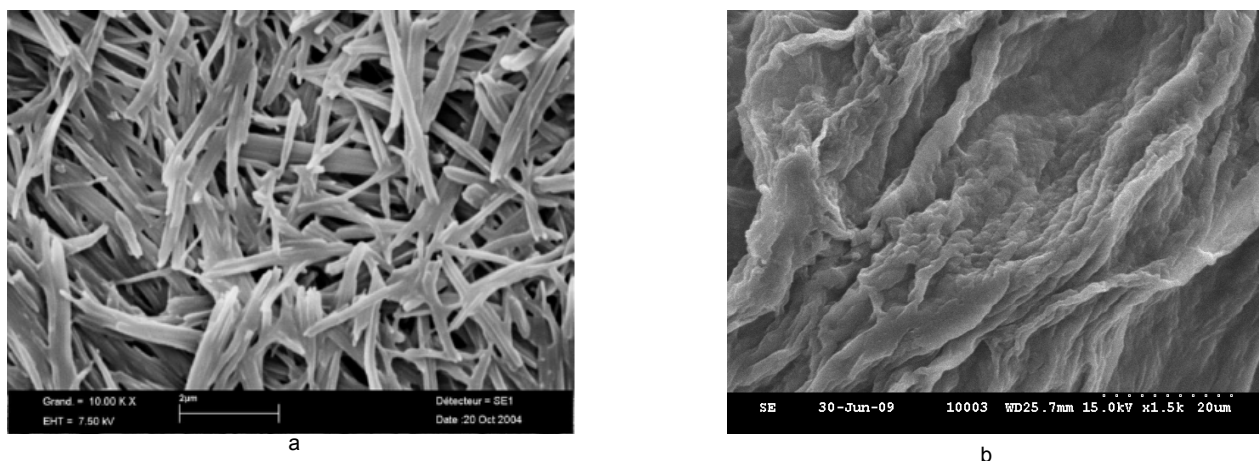
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Fig. 3 - Morphologies for xerogels obtained for DBS derivatives in different solvents / *Morfologiile xerogelurilor obţinute pentru derivaţii de DBS în diferiţi solvenţi* (a) **p-NO₂ -DBS/EtOH**; (b) **p-CH₃O-DBS/ dioxane**
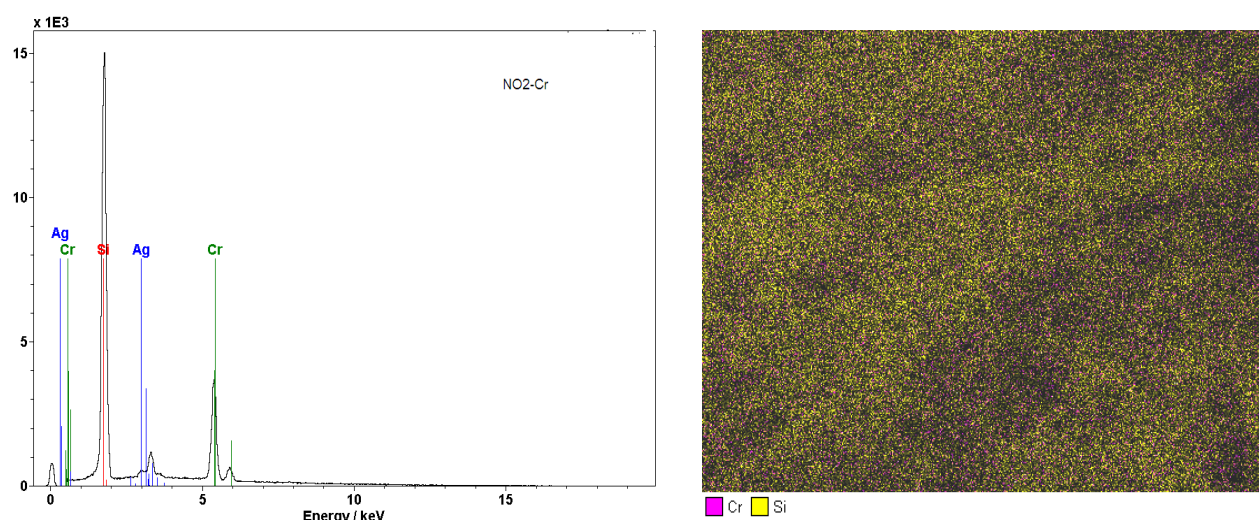

Fig. 4 - EDX spectra for the Cr-doped silica obtained by sol-gel polymerization of TEOS mediated by **p-NO₂ -DBS/CTAB/ MBA-Cr(CO)₃** system/ *Spectrul EDX al silicei dopate cu Cr obţinută prin polimerizarea sol-gel a TEOS mediată de sistemul p-NO₂ - DBS/CTAB/ MBA-Cr(CO)₃.*

The composition of the calcinated samples, from which all the organic compounds have been removed throught combustion, was determined by Energy Dispersive Spectrometry (EDX). EDX analyses revealed the presence of chromium accompanying silicium with an even distribution of chromium species on the silica fibers as presented, for example, for the case of Cr-doped silica obtained by sol-gel polymerization of TEOS mediated by **p-NO₂ -DBS/CTAB/ MBA-Cr(CO)₃** system (Figure 4).

The oxidation states of the Cr ions on the surface of the nanostructured synthesized silica were determined by X-Ray Photoelectron Spectra. In addition XPS was used to carry out a quantitative analysis of the Cr-doped silica samples by recording survey spectra in the binding energy range from 0 eV to 1200 eV (Fig. 5a). Distinct chromium, silicium and oxygen peaks were identified for all the investigated samples exhibiting a similar Si/Cr ratio, thus showing that the major

difference between them is the microstructure determined by the pair of **SDA** involved in every synthesis.

The peaks assigned for Cr2p profiles may be resolved by deconvolution in $Cr2p_{3/2}$ and $Cr2p_{1/2}$ components of Cr2p doublets. According to literature data [6,18] the dublet with binding energies of 577.29 eV and 587.05eV may be assigned to Cr^{3+} (from Cr_2O_3) as the major product (80%) while the corresponding dublet with 581.27 and 590.50 respectively to the minor product Cr^{6+} (mostly as cromate ion, CrO_4^{2-} or oligomers of it). Stoichiometry used in sol-gel polymerizations determine a chromium loading of ~10.0 wt%, concentration for which it is reasonable to expect some Cr_2O_3 clustering and partial Cr desorbtion from the silica surface as observed in SEM micrographs (Fig. 5b).
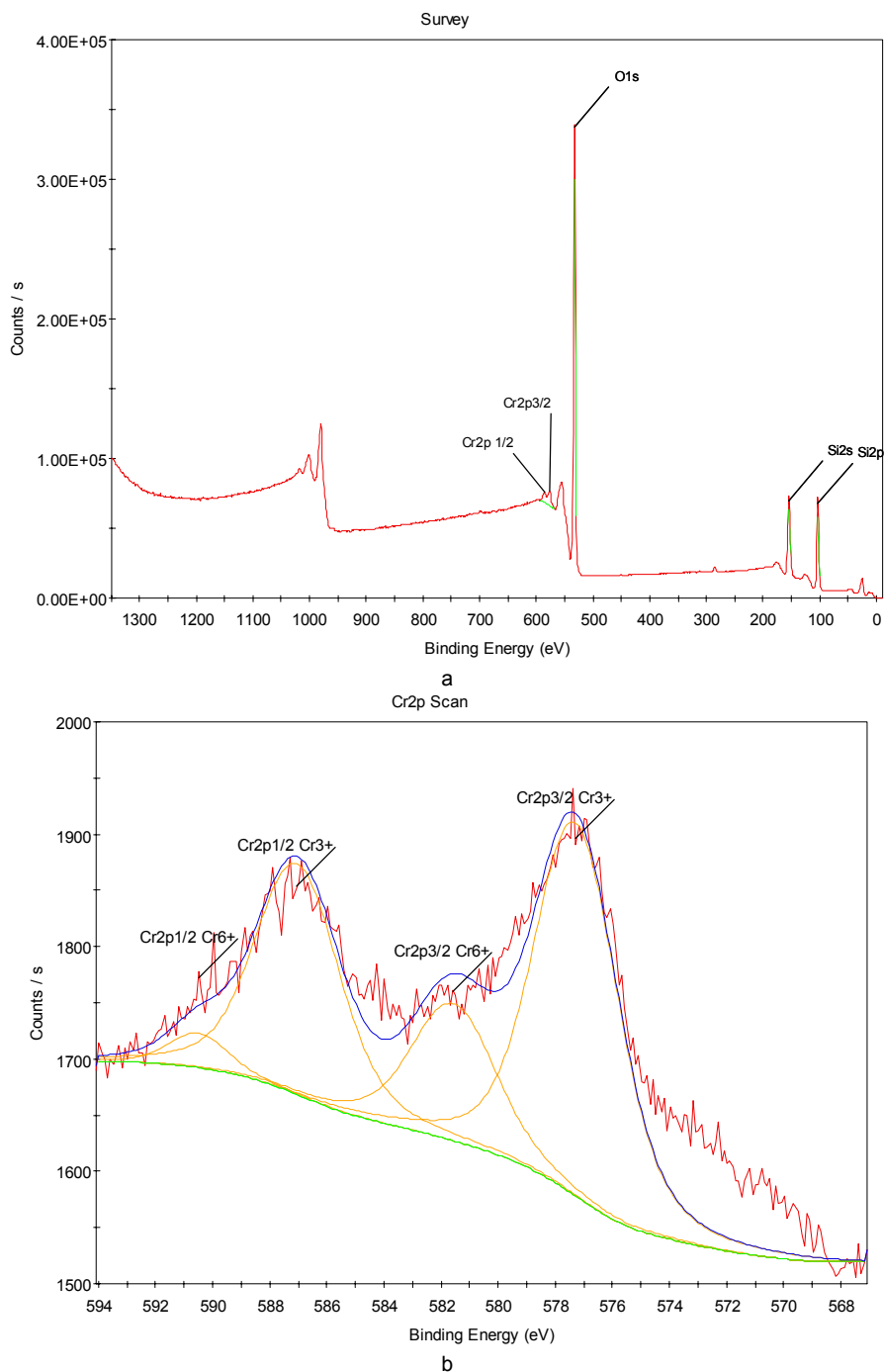
Fig. 5 -   XPS survey spectra(a) and high resolution XPS spectra (b) for the Cr- doped silica sample obtained by sol-gel polymerization
of TEOS mediated by *p-NO₂ -DBS/CTAB/ MBA-Cr(CO)₃* system / *Spectrele XPS de tip general (a) şi de rezoluţie înaltă (b) ale
silicei dopate cu Cr obţinută prin polimerizarea sol-gel a **TEOS** mediată de sistemul **p-NO₂ -DBS/CTAB/ MBA-Cr(CO)₃***

Table 2

Cr 2p 1/2 and Cr 2p 3/2 binding energies (eV) and proportion (%) of Cr^{3+} and Cr^{6+} ions for the Cr⁻
doped silica sample obtained via **p-NO₂ -DBS/CTAB/ MBA-Cr(CO)₃** system / *Energii de legatură pentru
Cr 2p 1/2 şi Cr 2p 3/2 (eV) şi proporţiile (%) în care se găsesc ionii Cr^{3+} and Cr^{6+} în proba de silice
dopată cu Cr obţinută cu sistemul **p-NO₂ -DBS/CTAB/ MBA-Cr(CO)₃***

Name *Tip de bandă*	Peak BE/ *Energie de legatură bandă,* eV	FWHM *Lărgimea liniei* , eV	At. % / *Procent atomic*
Cr2p3/2 Cr^{3+}	577.29	3.50	37.68
Cr2p1/2 Cr^{6+}	590.50	2.42	4.52
Cr2p3/2 Cr^{6+}	581.57	3.50	13.92
Cr2p1/2 Cr^{3+}	587.05	3.50	43.88

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4. Conclusion

Cr-doped silica with a chromium loading of 10.0 wt% were obtained by sol-gel polymerization of **TEOS** mediated by mixtures of structure-directing-agents, sorbitol-derived organogelators and **CTAB**, with a chiral 1-phenylethylamine-tricarbonyl-chromium complex acting both as catalyst and as a source of chromium. Morphologies of the silica samples are determined by two different transcription mechanism: formation of the siloxane granules mediated by the surfactant and aglomeration of the formed granules at the surface of the organogelator fibril. Organogelators that form xerogels with well-definite fibers (*e.g.* **p-NO$_2$ -DBS**) favor the the formation of hollow silica tubes while organogelators that form xerogels with closely-packed fibers (*e.g.* **p-CH$_3$O –DBS**) lead to a primary organization, aglomerated silica granules "necklace" type. Chromium ions are uniformly distributed on the silica matrix and consist of to Cr^{3+} (from Cr_2O_3) as the major product (80%) and Cr^{6+} as the minor product (20%, mostly as cromate ion, CrO_4^{2-} or oligomers of it). The high Cr/ SiO_2 loading (10wt. %) resulted from the stoechiometry of the polymerization reaction determines partial desorbtion of Cr from the silica surface and clustering as proved by XPS and SEM analyses.

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