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INFLUENCE OF TUBULAR TiO_2-ZrO_2 CERAMIC SUPPORT ON THE MORPHO-STRUCTURAL PROPERTIES OF THE UNDOPED AND Cu DOPED CARBON XEROGELS

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ABSTRACT. Undoped and Cu doped carbon xerogels with desired monolithic geometry were synthesized by sol-gel method followed by an ambient drying and a pyrolytic step. Resorcinol and potassium salt of 2,4-dihydroxybenzoic acid were used as precursors in polycondensation with formaldehyde to obtain undoped and Cu doped carbon xerogels, respectively. As reaction catalysts Na_2CO_3 and K_2CO_3, respectively were used. In order to enhance the strength of prepared materials, undoped and Cu doped carbon xerogels were synthesized into porous tubular TiO_2-ZrO_2 walls. The prepared samples were investigated by nitrogen adsorption, SEM, AFM and X-ray diffraction. Micro- and mesoporous carbon structures formed by interconnected carbon nanoparticles were obtained. In the case of Cu doped samples, homogeneous Cu nanoparticles dispersion into carbon xerogel matrix was observed. By synthesis of undoped and Cu doped carbon aerogels into ceramic wall, a decrease from macro- to micropores was observed.

Keywords: *sol-gel process, carbon xerogel, composite.*

INTRODUCTION

In the last decades, the technological development was based more and more on production and using of nanomaterial and nanocomposite with certain properties. In this context, various types of carbon materials are recognized as important materials in the field of catalysis [1,2], electrochemistry [3,4], adsorption [3,5], molecular sieve construction [6], etc.

Carbon xerogels (CX) are materials prepared by sol-gel process which present a high interest in material science [7-9]. Generally, the sol-gel synthesis of this material is based on the polycondensation of resorcinol with formaldehyde using Na_2CO_3 as catalyst [10]. Drying in ambient conditions of resulted RF gels followed by a pyrolysis treatment leads to carbon xerogels. Particular case of this material is metal doped carbon xerogel (Metal-CX)

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obtained by using the potassium salt of 2,4-dihydroxybenzoic acid as precursor, K_2CO_3 as catalyst and a metal salt aqueous solution as doping solution [11]. The useful characteristic of this synthesis way is morpho-structural controllability of material properties by changing of polycondensation parameters, mainly by ratios between precursors and catalyst or solvent [10-12]. The drying performed in ambient conditions is more economical advantageous than that performed in the supercritical conditions, which are used for aerogel synthesis.

In the case of applications for fluid separation/purification it was observed that is important to have strong molecular sieve membranes with exact geometric size and porosity [6]. Also, Cu based materials are known as catalyst for various chemical reaction such as water-gas shift reaction when H_2 is produced [13,14]. The presence of Cu species (Cu^0, Cu^{2+}) into membrane composition permits to achieve a combination between gas separation and catalytic activities.

The synthesis of CX or Cu-CX into macroporous commercial TiO_2-ZrO_2 ceramic support, stronger composites with both micropore structure and desire geometric dimensions were obtained. These composites, named CX/TiO_2-ZrO_2 and Cu-CX/TiO_2-ZrO_2, respectively present promising characteristics both for simply fluid separation and, in the case of Cu-CX/TiO_2-ZrO_2, for separation-catalytic applications.

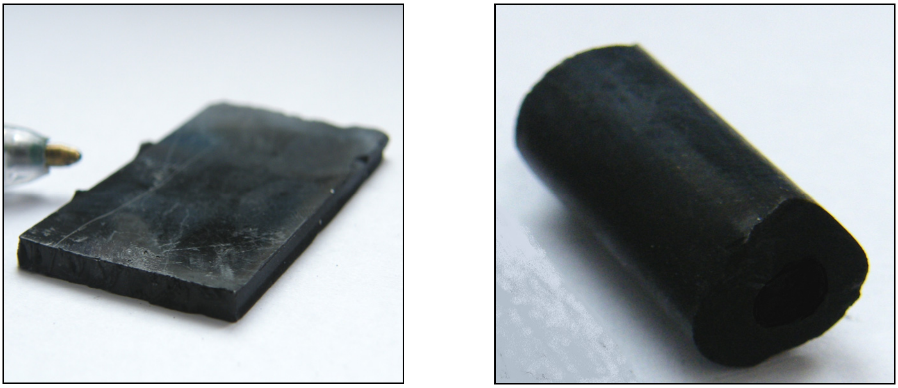
In this paper we present the study of the tubular TiO_2-ZrO_2 ceramic support influence on the morpho-structural properties of the undoped and Cu doped carbon xerogels. The morpho-structural properties were investigated by using nitrogen adsorption, SEM, AFM and X-ray diffraction.

RESULTS AND DISCUSSIONS

Synthesis of CX by sol-gel method based on polycondensation of resorcinol or potassium salt of 2,4-dihydroxybenzoic acid and formaldehyde allowed us to obtain various bulk geometry of monolithic samples according to the mould shape where reaction takes place (Figure 1). This property is very important in applications as electrode, supercapacitors or molecular sieve construction [3,4,6].

In the case of the unsupported CX, about 65% and 55% of volume shrinkage is observed during drying and pyrolysis steps, respectively. The volume variation can be adjusted by changing the synthesis parameters, mainly by modifying the ratio between the amount of precursors and catalyst or water used in the polycondensation process [10].

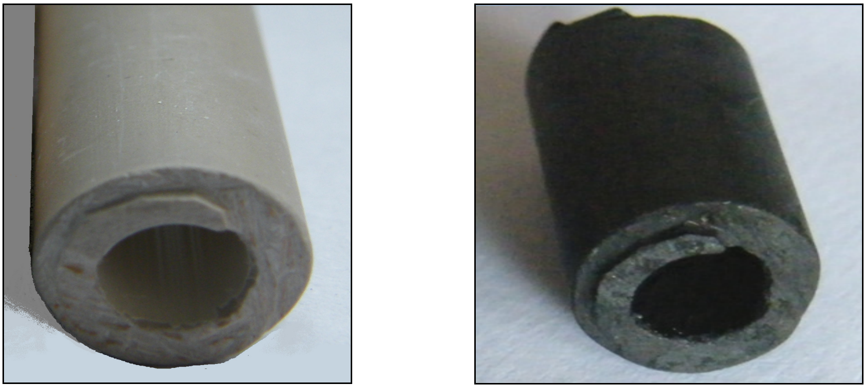
By performing the sol-gel process into porous ceramic supports, CX/ceramic material composite without structural shrinkage is obtained. In figure 2 a blank commercial TiO_2-ZrO_2 ceramic support (a) and a composite obtained by CX synthesized into TiO_2-ZrO_2 ceramic wall (b) are presented.



(a) (b)

Figure 1. Plate (a) and tubular (b) geometry of monolithic CX.

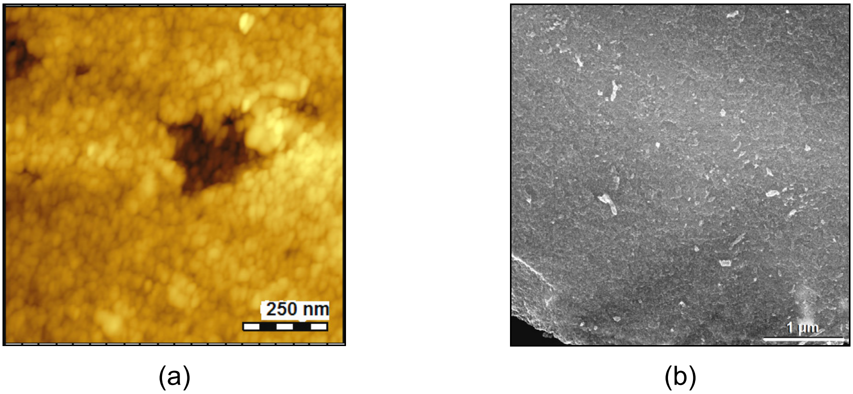
This strong composite type can be obtained with desired dimensions and applied, as molecular sieve by tightly placement into a steel reactor, for gas separation [6].



(a) (b)

Figure 2. Blank TiO_2-ZrO_2 (a) and CX/TiO_2-ZrO_2 (b).

A nanoporous structure of CX matrix with interconnected carbon nanoparticles in a size of tens nanometer is visualized by AFM (Figure 3a) and a carbon rough structure in a micrometer scale by SEM investigation (Figure 3b). In the case of Cu-CX the homogeneous dispersion of Cu nanoparticles with diameter around 65 nm into carbon framework is showed by SEM analysis (Figure 4).



(a) (b)

Figure 3. AFM (a.) and SEM (b.) images of CX.

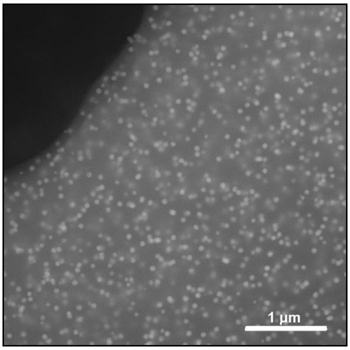


Figure 4. SEM image of Cu-CX.

The X-ray diffraction analysis of CX showed an amorphous structure represented by two large peaks at about $2\theta = 24^{o}$ and 44^{o} (Figure 5). A mixture between an amorphous and crystalline structure is observed for Cu-CX, with the same metal crystalline peak position such as in the case of corresponding Cu doped carbon aerogel [11,12]. A mixture between metallic Cu and Cu oxides is evidenced in metallic nanoparticles (Figure 5).

In case of xerogel/ceramic composite, a nanoporous structure of CX (Figure 6a) or Cu-CX (Figure 6b) which fills the macropore of TiO_2-ZrO_2 ceramic wall is showed by SEM. Also, a homogeneous Cu nanoparticle distribution into CX matrix is visualized for Cu-CX/TiO_2-ZrO_2 composite. A decrease of Cu % for obtained Cu doped composite compared with unsupported Cu-CX is observed (Table 1) by Energy-Dispersive X-Ray Spectroscopy (EDS) applied on the SEM investigated areas (see figures 4 and 6b).

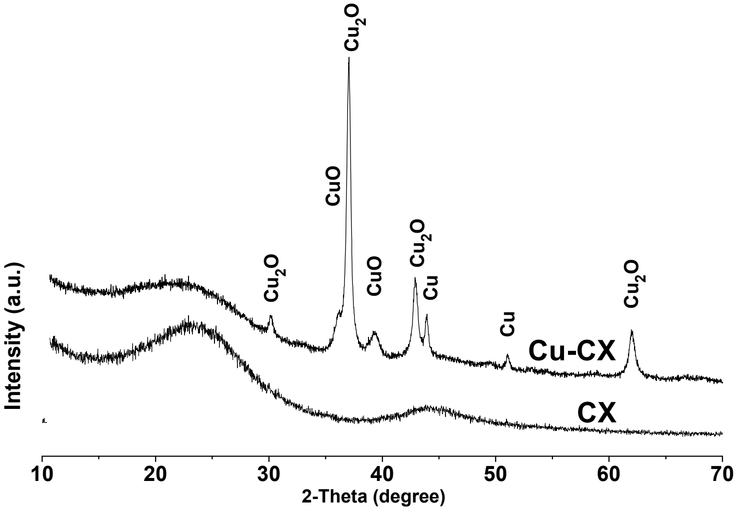
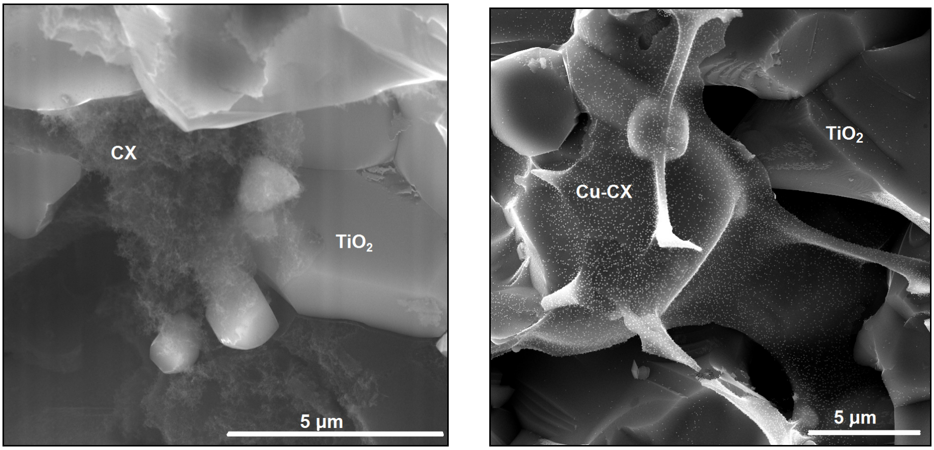


Figure 5. XRD patterns of CX and Cu-CX.

Higher BET surface areas and mesopore volumes are obtained by nitrogen adsorption on the unsupported samples than supported ones (Table 1). In the case of composite preparations, a decrease of the gelation time is observed. This phenomenon could be attributed to the presence of the ceramic support which promotes the increase of the branching of the carbon framework reflected in a decrease of both pore diameter and volume. Thus, the ceramic support can be considered as a second catalyst for the polycondensation reaction.



(a) (b)

Figure 6. SEM images of CX/TiO_2-ZrO_2 (a) and Cu-CX/TiO_2-ZrO_2 (b).

Table 1. Structure parameters and Cu concentration of prepared samples.

SAMPLES	S_{BET} [$m^2 g^{-1}$]	V_{meso} [$cm^3 g^{-1}$]	Cu %*
CX	78	1	-
Cu-CX	311	71	5.7
CX/TiO_2-ZrO_2	4	0.85	-
Cu-CX/TiO_2-ZrO_2	17	0.7	2.5

* Cu wt % was determined by EDS for the areas investigated by SEM

EXPERIMENTAL SECTION

Preparation of CX and Cu-CX

Undoped CX synthesis started with a resorcinol-formaldehyde wet gel preparation using resorcinol, *R,* (98 % purity), formaldehyde, *F*, (37 % solution), Na_2CO_3, *C*, (99.9 % purity), all from Aldrich, and bidistilled water, *W* [10]. Resorcinol (0.29 moles) is dissolved in bidistilled water at a *R*/*W* ratio of 0.2 g cm^{-3}. Solution of formaldehyde is added to the resorcinol solution (*R*/*F* = 0.5 molar ratio) under vigorous stirring. Afterwards, 0.1 M Na_2CO_3 aqueous solution is added to the previous prepared mixture (*R*/*C* = 500).

Cu-CX is prepared using as precursor the potassium salt of 2,4-dihydroxybenzoic acid obtained by neutralization of 2,4-dihydroxybenzoic acid, *A,* (99% purity, Aldrich) with K_2CO_3 (99%, Merck) in bidistilled water (*A*/K_2CO_3 = 2, *A*/*W* = 0.03 g cm^{-3}). To the obtained solution, formaldehyde (*A*/*F* = 0.5) and K_2CO_3, *K*, (*A*/*K* = 100) as catalyst are added.

The resulted solutions are placed in tightly closed glass moulds and cured at 70°C for 4 days. Two wet gel types are obtained: an undoped gel and a potassium doped gel. After a day of keeping in distilled water, the potassium doped gel is placed for one day in 0.1 M $Cu(NO_3)_2$ aqueous solution. After a new washing with acetone the next steps are ambient drying and pyrolysis in Ar atmosphere, at 750°C for 2 h. Monolithic undoped and Cu doped carbon xerogels are obtained.

Preparation of CX/TiO_2-ZrO_2 and Cu-CX/TiO_2-ZrO_2 composites

The xerogel/ceramic composite preparations are based on the same reactions and synthesis steps as in the case of unsupported undoped and Cu doped CXs, the difference consisted in the fact that TiO_2-ZrO_2 ceramic is introduced into the starting sol-gel solution. The commercial used TiO_2-ZrO_2 monochannel tube ceramic support (TAMI Industries) had the outer radius of 10 mm and tube wall thickness of 2.4 mm. The tube wall presents external

TiO_2 layer pore size distribution of 5 µm and a thin internal ZrO_2 layer of 3 nm. The sol-gel processes took place into the porous structure of the ceramic wall. The excess wet gel, from outside of ceramic wall, is removed before washing step. Very stable undoped or Cu doped CX/TiO_2-ZrO_2 ceramic composites were obtained after pyrolysis.

Morpho-structural investigations

AFM imagine was obtained with AFM-Agilent 5100. SEM images and EDS analysis were performed with a SEM-Quanta 200F microscope.

Specific surface area, pore size distributions, and pore volume determinations were performed by using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) calculation methods, with a Sorptomatic SO-1990 device. Before measurements the samples were degassed at 120 ^oC for about 12 h.

XRD patterns were recorded in θ - 2θ Bragg-Bretano geometry with a Siemens D5000 powder diffractometer having Cu-Kα incident radiation (λ = 1.5406 Å).

CONCLUSIONS

Very stable monolithic undoped and Cu doped carbon xerogel materials with desired shape but with a strong shrinkage were synthesized previously. The synthesis of CX and Cu-CX into porous TiO_2-ZrO_2 ceramic walls permits to obtain composite materials without shrinkage and interesting properties for molecular sieve construction. In addition, the strong fixation of Cu-CX into ceramic support and Cu nanoparticles into Cu-CX makes Cu-CX/TiO_2-ZrO_2 composite available for reactor-membrane construction.

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REFERENCES

1. Y. Yang, K. Chiang, N. Burke, *Catalysis Today*, **2011***, 178,* 197.
2. S. Cacchi, C.L. Cotet, G. Fabrizi, G. Forte, A. Goggiamani, L. Martín, S. Martínez, E. Molins, M. Moreno-Mañas, F. Petrucci, A. Roig, A. Vallribera, *Tetrahedron,* **2007**, *63*, 2519.
3. M. Inagaki, *New Carbon Materials*, **2009**, *24*, 193.
4. R. Sanjinés, M.D. Abad, Cr. Vâju, R. Smajda, M. Mionić, A. Magrez, *Surface and Coatings Technology*, **2011**, *206 15,* 727.
5. A. Maicaneanu, L.C. Cotet, V. Danciu, M. Stanca, *Studia UBB Chemia*, **2009**, *54 4*, 33.
6. D. Montané, K. Briceño, R. Garcia-Valls, in: D. Stolten, T. Grube (Eds.), *18th – World Hydrogen Energy Conference*, Essen, **2010**, *78-3*, 466.
7. L. Zubizarreta, A. Arenillas, A. Domínguez, J.A. Menéndez, J.J. Pis, *Journal of Non-Crystalline Solids*, **2008**, *354*, 817.
8. S. Morales-Torres, F.J. Maldonado-Hódar, A.F. Pérez-Cadenas, F. Carrasco-Marín, *Microporous and Mesoporous Materials*, **2012**, *153*, 24.
9. B.S. Girgis, I.Y. El-Sherif, A.A. Attia, N.A. Fathy, *Journal of Non-Crystalline Solids*, **2012**, *358,* 741*.*
10. L.C. Cotet, A. Roig, I.C. Popescu, V. Cosoveanu, E. Molins, V. Danciu, *Revue Roumaine de Chimie*, **2007**, *52*, 1077.
11. L.C. Cotet, M. Gich, A. Roig, I.C. Popescu, V. Cosoveanu, E. Molins, V. Danciu, *Journal of Non-Crystalline Solids*, **2006**, *352*, 2772.
12. L.C. Cotet, M. Baia, L. Baia, I.C. Popescu, V. Cosoveanu, E. Indrea, J. Papp, V. Danciu, *Jornal of Alloys and Compounds,* **2007**, *434-435*, 854.
13. R.J. Madon, D. Braden, S. Kandoi, P. Nagel, M. Mavrikakis, J.A. Dumesic, *Journal of Catalysis*, **2011**, *281, 1.*
14. K. Sagata, N. Imazu, H. Yahiro, *Catalysis Today*, **2012**, *in press,* http://dx.doi.org/10.1016/j.cattod.2012.03.064.