Influence of the Methodology Applied in the Formation Process of VO_x / Polyaniline Nanocomposites

Influência da Metodologia Aplicada no Processo de Formação de Nanocompósito VO_x / Polianilina

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ABSTRACT
The present work discusses the synthesis, characterization and thermoanalytical investigation of the hybrid material based on c-V2O5 and substituted polyanilines. 50 mL of an aqueous suspension with 0.5 g of oxide (2.75 mmol) in three concentrations of 2-methylaniline and 2-propylaniline (1.07 mmol, 5.49 mmol and 10.97 mmol) was prepared and submitted to high intensity pulse ultrasound. The goal was the investigation of the effect of the organic component used to modify the physical-chemical properties of the c-V2O5 by using TG-DTA, DSC, FTIR, DRX and SEM measurements. The results showed a higher degree of intercalation process for Poly (2-propylaniline) as well as a larger basal distance for same hybrid material.

Keywords: Nanohybrides VOx/Poly(substituted), sonochemistry, thermoanalytical investigation.

RESUMO
O presente trabalho discute a síntese, caracterização e investigação termoanalítica do material híbrido baseado em c-V2O5 e polianilinas substituídas. Foram preparados 50 mL de uma suspensão aquosa com 0,5 g de óxido (2,75 mmol) em trrês concentrações de 2-mtilanilina e 2-propilanilina (1,07 mmol; 5,49 mmol e 10,97 mmol) e submetidos a ultrassom de pulso de alta intensidade. O objetivo foi investigar o efeito do componente orgânico utilizado para modificar as propriedades físico-químicas do c-V2O5 por meio

de medidas de TG-DTA, DSC, FTIR, DRX e SEM. Os resultados mostraram maior distância basal para o mesmo material híbrido.

Palavras-chave: Nanohíbridos VOx / Poly(substituído), Sonoquímica, investigação termoanalítica

1 INTRODUCTION

Oxide nanomaterials with lamellar structures and polymeric organic components represent a new class of materials (nanocomposites) with improved physical-chemical properties compared to the pristine oxide (Zarbin, 2007; Huang et al., 2019; Xia et al., 2019). The synthesis of these nanomaterials has been object of a lot of discussion in the literature due to a great number of applications, e.g., energy conversion devices (secondary batteries) which work at room temperature (Majumdar & Ghosh, 2021; Meng et al., 2019; Tang et al., 2018). Among the inorganic precursors which possess appropriate structures, lamellar materials stand out such as tungsten oxides and vanadium pentoxide (Canepa et al., 2017; Massé, Uchaker, & Cao, 2015; Liu et al., 2012; Gautam, Canepa, Richards, Malik, & Ceder, 2016; Cheng et al., 2016; Oliveira, Torresi, & Torresi, 2000; Livage, 1992; Braithwaite, Catlow, Gale, & Harding, 1999; Schoiswohl, Surnev, Netzer, & Kresse, 2006). For the organic ones, there are the intrinsically conductive polymers (ICPs) such as polypirrole, polythiofene and polyaniline (Shirakawa, Louis, Macdiarmid, Chiang, & Heeger, 1977; Malta, Silva, Galembeck, & Korn, 2008; Huguenin, & Torresi, 2008; Shao, Jeon, & Lutkenhaus, 2013). Few works refer to substituted anilines to produce ICPs, specifically the poly(2-methylaniline) (PMethyl) and poly(2-propylaniline) (PPropyl). The absence of information increases when it is referred to the hybrid systems VO_x/(PMethyl) and VO_x/(PPropyl) synthesized by ultrasound. In addition, no study has been accomplished seeking to explore the thermal stability of those matrices, identification of the obtained products and the energy homogeneity involved by TG-DTA and DSC measurements. Thus, this work had as objective to investigate the termal behavior and the influence of the applied methodology in the formation process of nanocomposites, VO_x/PMethyl and VO_x/PPropyl.

2 MATERIALS AND METHODS

2.1 SAMPLES PREPARATION

Initially, it was added 0.5 g (2.75 mmol) of crystalline V_2O_5 in 50 mL of deionized water. To this suspension a volume of 115 µL 2-methylaniline was placed (1.07 mmol).

Then, the sonochemistry route was applied using the methodology established by Malta, Silva, Galembeck, & Korn (2008) with some changes, substituting the continuous way for the pulse one. In that case, to each 10 s of ultrasound, a break of 1 s was kept between the cycles. Later, the sample was filtered under vacuum using cellulose acetate filter with porosity of 0.45µm, washed with ethanol until evaporation. The same procedure was repeated for the volumes of 115, 587 and 1176 µL using the same amount (1.07, 5.49 and 10.97 mmol) of 2-propylaniline.

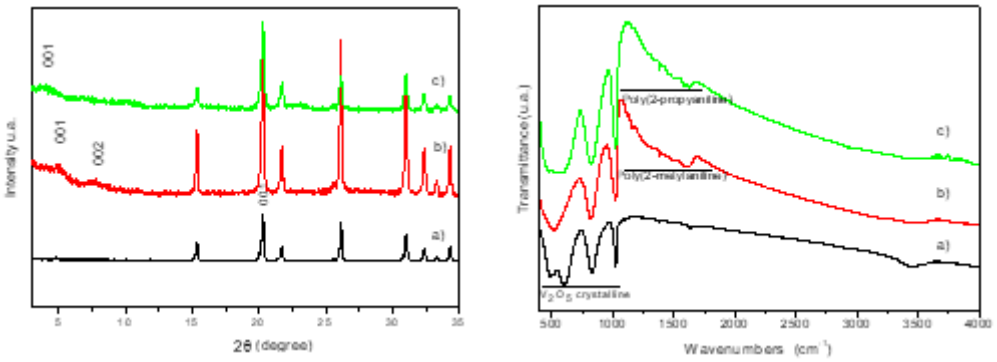
2.2 SAMPLES CHARACTERIZATION

The spectra of FTIR were obtained using a Spectrum 100S Perkin Elmer equipment. The crystalline phases were identified for X-ray powder diffraction in a Shimadzu XRD-6000. The images of scanning electronic microscopy of samples were obtained using Amray model 1860 FE SEM equipment. The TG/DTA experiments were accomplished in dynamic atmosphere of air and nitrogen (50 mL min^{-1}) from 25 °C to 1000 °C at a rate of 10 °C min^{-1} and sample mass around 8 mg using a Shimadzu TGA-60. The DSC experiments were accomplished in dynamic nitrogen atmosphere (50 mL min^{-1}) from 25 °C to 600 °C, the same heating rate used for TG/DTA experiments and sample mass around 2 mg using the Shimadzu DSC-60 modular system.

3 RESULTS AND DISCUSSION

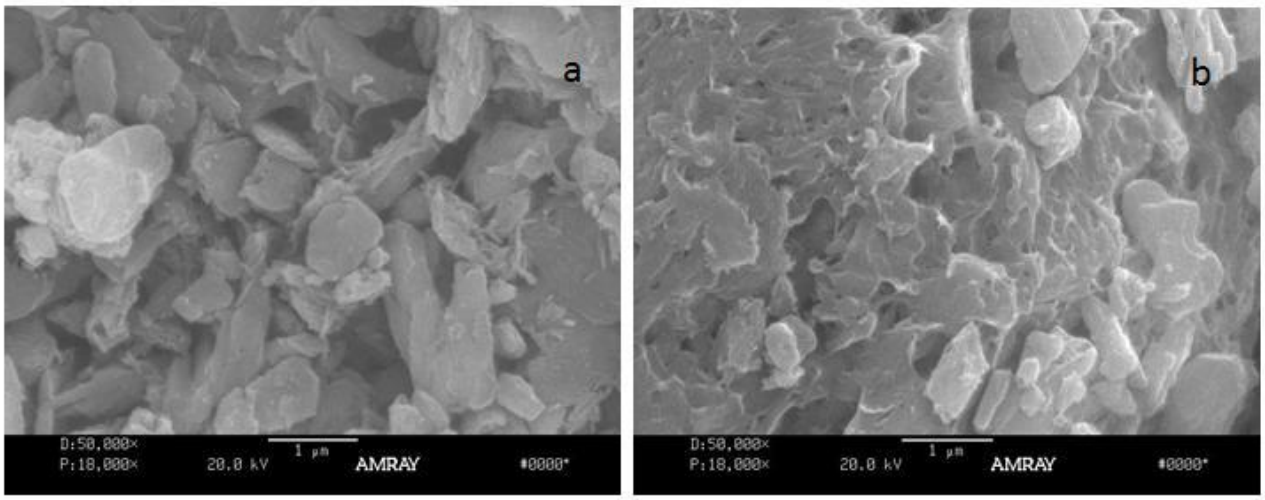
All the samples presented an intense green coloration suggesting presence of polyanilines and/or mixed sites of V^{4+}/V^{5+}. This fact is confirmed by DRX experiments which shown a discrete presence of the peaks 001 and 002 in regions at low angles (between 3.80 and 5.10 degrees) indicating partial formation of the composites of VOx/PMethyl and VOx/PPropyl (see Figure 1 (b) and (c)). These peaks at low angles can be related with intercalation of polymer between oxide layers, that increase the basal distance. FTIR experiments (Figure 1, right) also confirmed a partial conversion of vanadium oxide in VO_x/PMethyl and VOx/PPropyl due to discrete bands related to the polymer component. These FTIR spectra can be divided in two regions: below 1000 cm^{-1} which correspond oxide vibrations and between 1100 and 1800 cm^{-1} related to polymer IR absorptions.

Figure 1. Powder XRD and FTIR (right) of the samples: a) c-V2O5, b) VOx/PMethyl, c) VOx/PPropyl.



SEM images (Figure 2) revealed that both composites presented heterogeneous plate morphologies, very different from nanocomposite produced by Malta, Silva, Galembeck, & Korn (2008) obtained during acoustic cavitation in continuous mode.

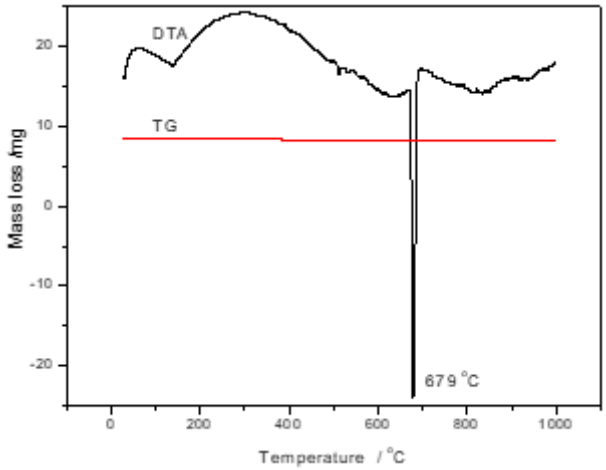
Figure 2. SEM images composites (magnification 50000x): (a) VO_x/PMethyl and (b) VO_x/PPropyl.



This result reinforced the idea of partial conversion, discussed previously in DRX, FTIR and that will be corroborated by the data TG presented below.

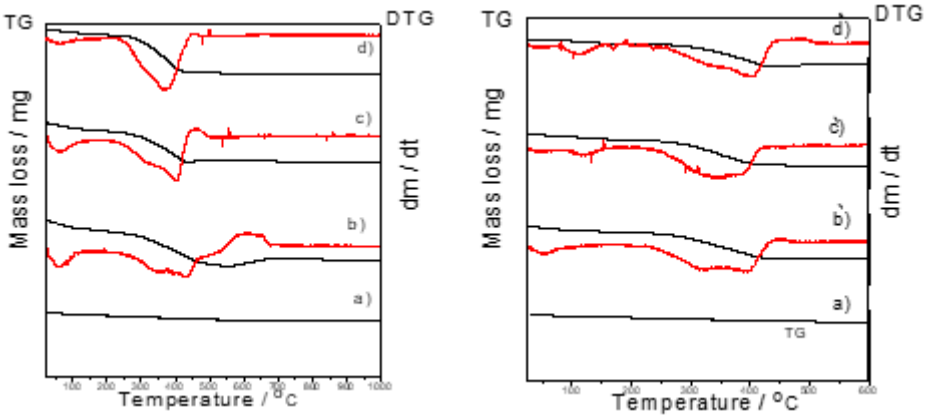
Figure 3 show results of TG/DTA for the crystalline vanadium oxide. This sample presents two endothermic events at 150 °C and 679 °C ascribed to the presence of small amount of superficial water and fusion of the oxide, respectively.

Figure 3. Curves TG/DTA of the V_2O_5 crystalline.



TG/DTG analyses are shown in the Figure 4. A decreasing of mass between 100 and 152 °C can be attributed the evaporation of water and possible liberation of unreacted 2-metylaniline. Between 152 - 700 °C ocurr thermal decomposition of polymer in two consecutive stages.

Figure 4. Curves de TG/DTG of the samples on the left: a) V_2O_5 crystalline, b) VO_x/PMethyl-1, c) VO_x/PMethyl-2, d) VO_x/PMethyl-3 and the right: b') VO_x/PPropyl-1, c') VO_x/PPropyl-2, d') VO_x/PPropyl-3.



In the first stage it is reasonable to consider the decomposition of polymers with small molecular weight and/or polymers linked to the surface of vanadium oxide. For the second decomposition stage, probably occurs the degradation of polymers with longer chains (higher molecular weight) and/or polymer chains deeply intercalated in vanadium oxide. This fact can be supported by the higher initial degradation temperature for samples with larger amount of organic component used in the synthesis process. In summary, for samples with higher organic concentration (large amount of nanocomposites), it is observed higher thermal stability for final products. This fact occur

due to the synergistic effect between inorganic/organic materials, which increases the thermal properties of products formed Lira-Cantu, & Gomez-Romero, 1999; Englebienne, & Hoonacker, 2005; Romero, 2001).

The table below shows the variation of energy values assigned to the events that characterized the exothermic decomposition of the organic matrices.

Table 1. variation of energy of the nanohybrides.

	2ª steps			**3ª steps**		
Samples	ΔT_2 (ºC)	ΔM_2 (%)	ΔH_2 (J/g)	ΔT_3 (ºC)	ΔM_3 (%)	ΔH_3 (J/g)
VOx/PMetyl-3	125.72	5.296	-105.84	129.68	11.559	-232.33
VOx/PPropyl-3	118.39	4.535	-151.10	93.55	6.604	-75.41

Therefore, these results corroborated with previous DRX and FTIR experiments indicating a (partial) formation of nanocomposites, as previously discussed. Finally, the increase of mass observed mass in the last stage of the thermodecomposition process, correspond to, possibly to the oxidation of some V^{4+} to V^{5+} sites, forming the initial c-V_2O_5 structure:

$$2\,VO_x + 1/2\,O_2 \longrightarrow V_2O_5$$

Therefore, the final product of thermal decomposition of the Vox/Methylpolyaniline sample, obtained at 800 °C by TG, refers to the same starting material c-V_2O_5. Recently, it was proposed by Channu et al. (2010) that after the decomposition of polymeric matrices of PVP and PVA blends, occur a change in the coordination environment of the metal centers of the oxide (change in oxidation state) which is responsible for the event of gain of mass.

4 CONCLUSIONS

The synthesis process using low frequency ultrasound in pulse mode partially converted the matrices c-V_2O_5/Methylaniline and c-V_2O_5/Propylaniline into oxide nanomaterials. A higher conversion was evidenced for VO_x/PMethyl while there was a larger basal detachment for VO_x/PPropyl. The TG-DTA and DSC results indicated that the amount of water is intimately linked to the hydrophobic character of the samples

showing lower value of mass loss for the VO_x/PPropyl hybrid. During the decomposition, exothermic processes were observed for the VO_x/PMethyl samples attributed to larger amounts of polymer intercalated that also justifies a larger thermal stability for this material. Besides, the TG results showed mass increase due to the change of VO_x into V_2O_5 caused by the oxidation of some V^{4+} into V^{5+} sites present in the hybrid sample. Thus, the thermal analysis had a fundamental contribution for reinforcing the DRX, FTIR and SEM results.

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