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Synthesis and Characterization of Intercalate Phases in the Organic–Inorganic Polyaniline/V_2O_5 System

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The synthesis, and spectroscopic and structural characterization of a series of hybrid PAni/V_2O_5 materials are reported. We have performed a systematic study of the synthesis of the hybrids by direct *in situ* reaction of aniline with V_2O_5 hydrogels and have determined key parameters for the reproducibility of the materials obtained. We have established the existence of two phases in the PAni/V_2O_5 system corresponding to the intercalation of one and two monolayers of PAni into V_2O_5. The characterization of these materials includes FTIR spectroscopy, X-ray diffraction, Thermogravimetric analyses, and resistivity measurements. © 1999 Academic Press

INTRODUCTION

Vanadium pentoxide gels constitute ideal hosts for the intercalation of a large variety of species, both organic and inorganic (1–20). These materials are amorphous or poorly crystalline gels which are truly inorganic polymers prepared by the acidic condensation of the vanadate anion (21). We can consider three major kinds of intercalation processes into these acidic V_2O_5 gels: first, those involving redox reactions, with intercalation of cationic species to compensate for the reduction of V_2O_5; second, the processes involving acid–base reactions; and finally, ion-exchange processes or intercalation of neutral guests which would keep unchanged the charge of the host.

The intercalation and subsequent polymerization of aniline into V_2O_5 gels involves a combination of acid–base and redox reactions. Earlier studies on this system have included the reaction of anilinium iodide with films of V_2O_5 xerogels (11, 14) but the most frequently used synthesis involves the reaction between aniline and preformed films of dry V_2O_5 xerogels. (6, 10, 12, 16, 17, 20, 22) The only case we have found in the literature of a direct reaction between aniline and bulk samples of a V_2O_5 hydrogel was a brief allusion to a single sample within a more general discussion on PAni intercalation in V_2O_5 films (23).

As part of our current effort in the synthesis of hybrid organic-inorganic electroactive materials (24–33) and their application in lithium reversible cells we have carried out a systematic study of a modified synthesis for the preparation of bulk samples of the hybrid PAni/V_2O_5 by direct reaction of aniline with V_2O_5 hydrogels (26, 28). We present here the results of this study, the optimization of synthesis, and further treatments of the hybrids. We will analyze their thermal and structural stability and present evidence for the existence of two distinct phases of adducts in this organic–inorganic system.

EXPERIMENTAL

Reagents

KBr FTIR grade 99 + % and aniline 99.5% were purchased form Aldrich. H_3PO_4 85% and H_2SO_4 96% were obtained from Panreac, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ 99.9% was from Carlo Erba. $NaVO_3$ 99.5% and the ion-exchange resin DOWEX 50 × 2–100 were purchased from Sigma. Aniline was distilled under vacuum before use, all other reagents were used as received.

Measurements

A Carlo Erba CHN EA 1108 system was used for elemental analyses. Vanadium (V) in the gel was analyzed by a potentiometric titration method described elsewhere (34) with a CRISON potentiometer. Vanadium content in the final hybrid material was analyzed after complete calcination of the organic part by atomic absorption spectroscopy in a Perkin Elmer 2100 apparatus. The electric resistivity of pelletized samples was measured by the Van der Pauw technique (35) with a HP 2432 multimeter, and samples of the materials were dried under dynamic vacuum until constant weight and pressed into pellets onto which four copper leads were attached with silver paint. Infrared spectra were recorded as KBr pellets with a Nicolet 710

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TABLE 1
Chemical Analyses Performed to the Hybrid PAni/V_2O_5 Materials Synthesized with Different Aniline/V_2O_5 Nominal Ratios

		An:V_2O_5[a]	%C	%N	%H	%V	N/V_2O_5	%H_2O[b]	Formula[c]
e	Exp.	14:1	28.88	5.48	1.45	33.57	1.2	3.00	
	Calc.		28.92	5.62	1.96	34.07			$(C_6H_4N)_{1.2}V_2O_5\cdot 0.50H_2O$
d	Exp.	11.5:1	27.47	5.21	1.40	34.98	1.1	1.98	
	Calc		27.64	5.37	1.77	35.53			$(C_6H_4N)_{1.1}V_2O_5\cdot 0.32H_2O$
c	Exp.	8.6:1	16.49	3.29	0.41	41.10	0.58	3.05	
	Calc		17.31	3.36	1.31	42.18			$(C_6H_4N)_{0.58}V_2O_5\cdot 0.41H_2O$
b	Exp.	5.7:1	17.12	3.35	0.71	40.95	0.60	3.19	
	Calc		17.73	3.45	1.36	41.78			$(C_6H_4N)_{0.6}V_2O_5\cdot 0.44H_2O$
a	Exp.	3:1	14.04	2.63	0.56	42.29	0.45	5.63	
	Calc		13.76	2.67	1.40	43.22			$(C_6H_4N)_{0.45}V_2O_5\cdot 0.74H_2O$

[a] Nominal aniline:V_2O_5 ratio used in the reaction.
[b] Determined by the TGA weight loss from room temperature to 120°C.
[c] Water contents calculated from %H_2O (TGA).

FTIR spectrophotometer. Thermal treatments under oxygen were performed in a Perkin Elmer TGA7 thermogravimetric balance with a heating rate of 1°C/min. Powder X-ray diffraction analyses were performed in a Rigaku Ru-200B diffractometer from $2\theta = 3$ to 60° with Cu$K\alpha$ radiation. Electrochemical studies were carried out with a computer-controlled EG&G PAR270A potentiostat/galvanostat on a three-electrode cell with Ag/AgCl reference electrode and Pt counterelectrode for characterization in aqueous media.

RESULTS AND DISCUSSION

Synthesis of PAni/V_2O_5 Hybrids

We have carried out a series of synthesis experiments where the molar ratio of aniline/V_2O_5 was varied from 3 to 20. The exact nominal values were as follows: sample (a) 3, (b) 5.7, (c) 8.6, (d) 11.5, (e) 14, (f) 17, and (g) 20 mole of aniline per mole of V_2O_5. The synthesis was performed as follows: The corresponding amounts of aniline were dissolved with constant stirring in 50 ml of distilled water and that solution was slowly added to a colloidal dispersion of 24 ml of V_2O_5 0.16 M (3.84 mmol) in water (50 ml total volume), which had been previously aged for 1 month. An instant color change of the solution from red to dark green was observed, indicating reduction of V_2O_5 and oxidation of aniline. The reaction was kept with constant stirring for 1 h. During this time the viscosity of the mixture increased until a solid precipitate was formed. The final morphology of the precipitate depended upon the amount of aniline used in each case. After the reaction was complete the solid was filtered off and washed repeatedly with water until total elimination of the initial light yellow color in the filtrate.

In principle we expected to obtain a series of hybrids with PAni contents increasing proportionally to the nominal amounts of aniline used during the syntheses. However, contrary to these expectations, chemical analyses (Table 1) showed that our samples could be grouped into two sets (see Fig. 1), one with ca. 0.5–0.6 aniline rings per V_2O_5 (samples a–c) and another with double that amount; i.e., 1.1–1.2 rings per V_2O_5 (samples d–e). Samples f and g were not homogeneous, apparently contained excess aniline, and were not considered for chemical analyses.

Effect of Reaction Times on the Materials Obtained

The final structure and morphology of the hybrid PAni/V_2O_5 materials are found to depend on the period of time employed in the polymerization reaction. Figures 2a–2e show the diffraction patterns obtained for the hybrid PAni/V_2O_5 (for a sample with a nominal Ani/V_2O_5 ratio of 3:1) synthesized during different periods of time and for the pure V_2O_5 xerogel (Fig. 2f). The separation between V_2O_5 layers is given by the position of peak 001 (7.78 for the pure xerogel material). After hybrid PAni/V_2O_5 synthesis this peak shifts to lower 2θ values, indicating a larger distance

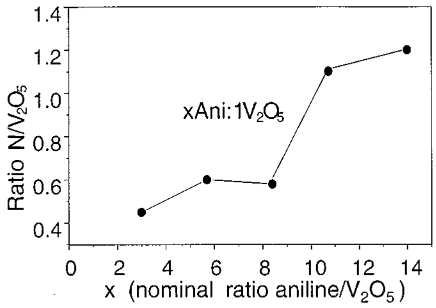


FIG. 1. Relationship between the nominal ratio of aniline to V_2O_5 used in the reaction and the actual ratio obtained from nitrogen and vanadium chemical analyses.

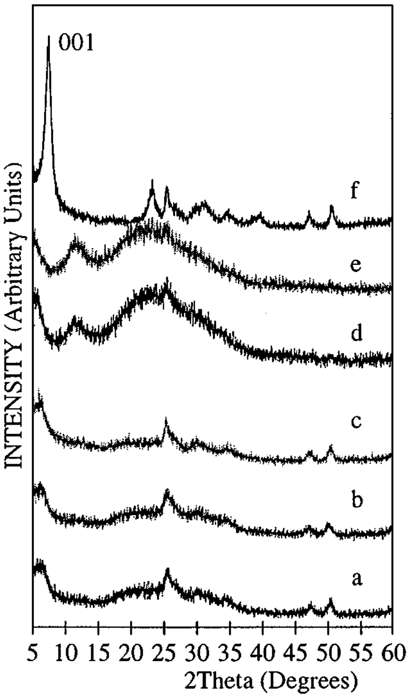


FIG. 2. Powder X-ray diffraction patterns corresponding to hybrid PAni/V_2O_5 materials synthesized during different periods of times. (a) 10 min, (b) 1 h, (c) 24 h, (d) 72 h, and (e) 194 h.

between layers. This behavior corresponds to the intercalation of large size molecular material such as PAni. For relatively short periods of time the structure of the hybrid seems to be mostly determined by the V_2O_5 network. Peaks of the inorganic oxide gel are apparent and a broad diffuse scattering feature is the sign of PAni intercalation. For longer reaction times, peaks from the inorganic component are almost completely obscured by an emerging diffuse scattering pattern with two maxima in 2θ at 12° and 22° associated with the growth and dominance of the organic polymer network.

It should be noted that the 001 peak for materials obtained after long reaction times is only slightly shifted with respect to that of materials prepared for only a few hours. This small shift corresponds to an expansion of the interlayer spacing of 1–2 Å, far from the 6-Å expansion associated with intercalation of a second PAni chain (see below). This indicates maybe some reorganization of the PAni chains in the intercalate but not an intercalation of a substantial additional amount of PAni. In good agreement with this, the most evident feature of XRD patterns of samples reacted for long times is the growth of the broad diffuse scattering peaks which can be associated with the short-range order of the polymer chains (Figs. 2d and 2e). These data show how the materials obtained after 3 or more days of reaction have essentially the same PAni/V_2O_5 ratio but present a structure where the V_2O_5 host structure has been partially taken over by the structure of PAni. In other words, the long-range order of V_2O_5 indicated by diffraction peaks has decreased and the order associated with PAni has increased.

The microstructure of these materials is also dependent on reaction times. Figure 3 shows SEM photographs corresponding to PAni/V_2O_5 hybrids synthesized during different periods of time. We can see a clear difference in particle size between the samples, with smaller sizes found for samples reacted during longer periods of time.

Effect of Reaction Temperatures on the Materials Obtained

The temperature of the reaction mixture during synthesis affects directly the organic part of the hybrid PAni/V_2O_5. We studied the effect of reaction temperature on the PAni/V_2O_5 hybrids obtained. The synthesis was carried out at temperatures of 0°C, room temperature, and 55, 100, and 120°C. For these experiments all other reaction conditions were kept constant as described before: V_2O_5 previously aged for 1 month, nominal aniline/V_2O_5 ratio of 3:1, reaction time 1 h, and vacuum drying at ambient temperature. Powder X-ray analyses performed to each of the resulting samples showed no significant difference between them. FTIR spectra of samples prepared at different temperatures showed some variation of the intensities of peaks at 1400–1600 cm^{-1} (see Fig. 4) which were nevertheless difficult to assign to specific structural features of the polymer. On the other hand, some degradation of polyaniline is indicated by the physical and electrochemical properties, which include the electrical conductivity of the materials (see Fig. 5c) and especially the electrochemical activity associated with polyaniline, both of which decrease for samples prepared at higher temperatures (25, 26).

From this point of view the best materials are therefore the ones prepared at lower temperatures; this is a trend already observed in other conducting organic polymers (33). In the present case the highest conductivity (0.01 S/cm) corresponds to a sample prepared at 0°C

Electrical Conductivity

We carried out systematic measurements of resistivity for the hybrid PAni/V_2O_5 materials obtained in order to correlate them with the synthesis conditions. Figure 5 shows conductivity values for samples synthesized with different aniline/V_2O_5 ratios (a), reaction times (b), and reaction temperatures (c).

For samples synthesized with different nominal aniline/V_2O_5 ratios the conductivity values varied from 10^{-2} to 10^{-6} S cm^{-1} (Fig. 5a), the higher values corresponding to the samples with a smaller amount of aniline in the reaction mixture. The low conductivity of samples obtained with greater excess of aniline could be due to the basic medium

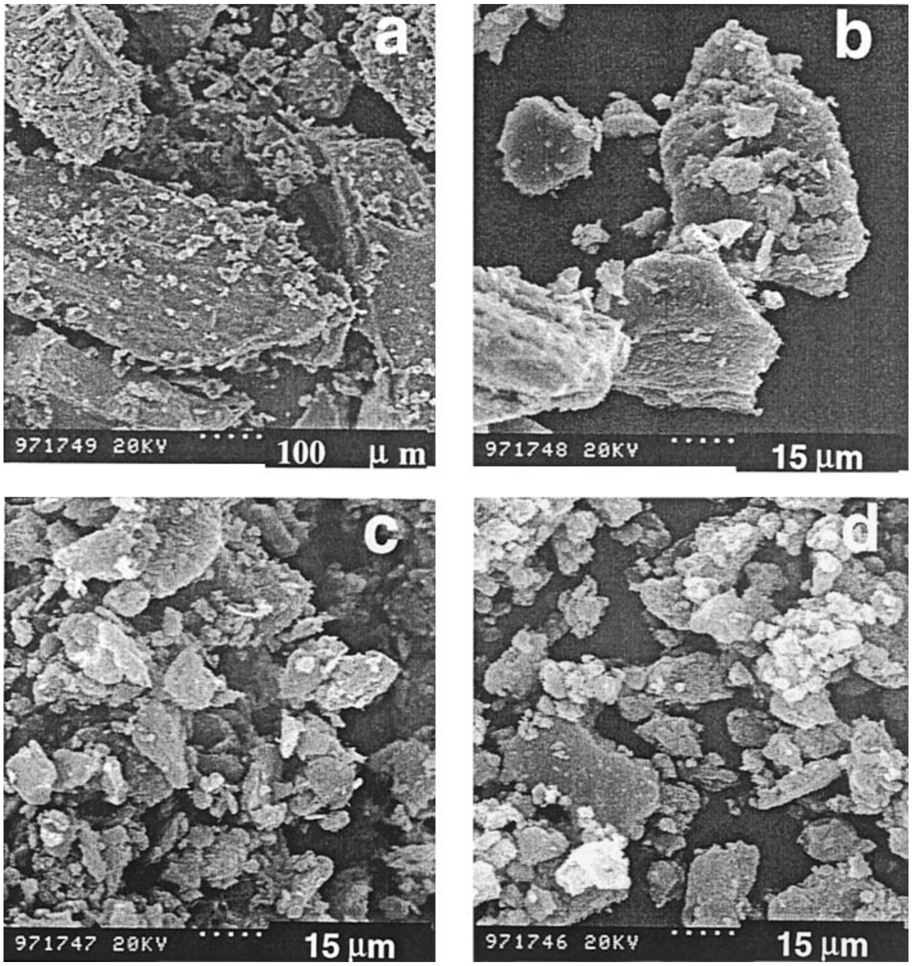


FIG. 3. SEM photographs of hybrid PAni/V_2O_5 materials synthesized during different periods of time: (a) 1 h, (b) 24 h, (c) 72 h, and (d) 194 h. The scale corresponds to 100 µm for (a), and 15 µm for (b), (c), and (d).

derived from that large excess. Such basic medium could lead to a larger number of unprotonated aniline units, in its undoped form or even polymerized -meta, all of which would result in poorly conducting PAni chains.

On the other hand, our work shows an increased conductivity for materials prepared during longer times (Fig. 5b). In this case the increase in conductivity is probably due to a continued process of growth of the organic polymer network, as evidenced from X-ray diffraction patterns in Fig. 2 above. Short PAni chains could thus couple within the inorganic framework even many hours after their intercalation. The chains would slowly get longer, leading to a larger conductivity. Additionally, longer reaction times also lead to smaller particle size (as shown in the SEM photographs in Fig. 3) and this could result in better grain connectivity in pellets and consequently an improved conductivity. Electrical conductivity of the hybrid materials directly depends on polymer stability. It is well known that conducting organic polymers in contact with air tend to reach a thermodynamically favored state characterized by a lower electrical conductivity (33).

Finally samples prepared at different temperatures (Fig. 5c) show a decreasing trend in conductivity as reaction temperature increases. This must be associated with the degradation of the conducting organic polymer at mildly high temperatures as pointed out above from FTIR spectra (Fig. 4).

Phases in the System PAni/V_2O_5

At the beginning of this section we saw how our hybrid materials prepared with different nominal ratios of aniline: V_2O_5 (samples a to g) could be classified into two groups according to their *real* contents of PAni. There were samples with 0.5–0.6 rings per V_2O_5 (a–c) and the others with double that amount.

In what follows we will present further studies to characterize the materials obtained from the different nominal

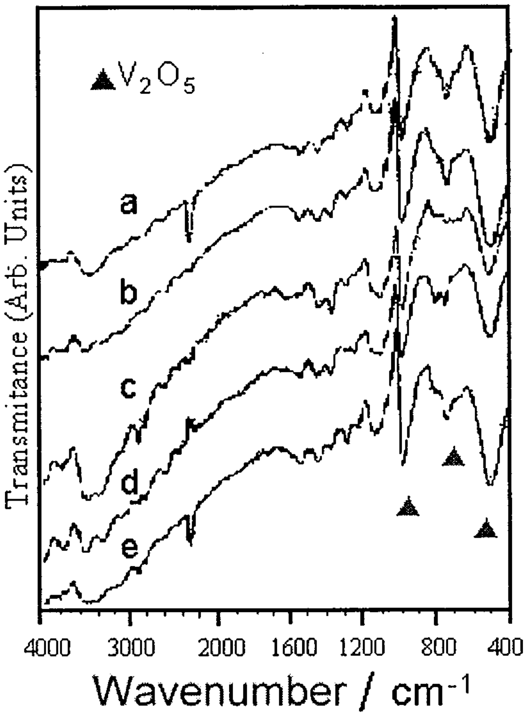


FIG. 4. FTIR spectra of the hybrid PAni/V_2O_5 synthesized at different temperatures: (a) 0°C, (b) room temperature, (c) 55°C, (d) 100°C, and (e) 120°C. Triangles mark the peaks assigned to V_2O_5.

ratios. We have used thermogravimetric analyses, infrared spectroscopy, and X-ray diffraction.

We have used TGA analyses with a double purpose. First of all it constitutes a study of the thermal stability of the samples; second, it serves as an analytical technique, allowing the determination of the percentage of organic matter and water in our samples. Figure 6 shows the thermogravimetric analyses performed on the series of samples a through e. First of all, The thermograms show variable amounts (3–5%) of weakly bound water (lost at temperatures below 120°C). These losses have been used to calculate the water contents for each sample (indicated in Table 1). Between 120 and 425°C the weight loss must be assigned to the decomposition of the organic polymer plus possibly a loss of strongly bound water or oxygen functional groups (-OH=O) attached sometimes to conducting polymer rings by oxidative addition of oxygen competing with the oxidative polymerization. Comparison of TGA weight loss with the percentage of organic matter from chemical analyses allows the extraction of two conclusions: First, there is a very good correlation between both series of data (Fig. 7), and samples clustered around the two mentioned chemical compositions also show in the TGA. Second, there is a very small systematic deviation (TGA losses are 1–2% units larger than organic matter from chemical analyses), which could correspond to a small amount of tightly bound water or to oxygen impurity groups present already in the polyaniline chains. In view of the systematic deviations between experimental and calculated chemical analyses (see Table 1) the second explanation (just oxygen loss) is favored.

It is well known that water in V_2O_5 xerogels has a negative effect on the specific charge and cyclability characteristics of that material as cathode in lithium batteries(36). Polyaniline intercalation into the V_2O_5 framework has been proposed to remove some of these water molecules (22). Our work confirms this observation and provides further details about the amount and nature of that displaced water.

Figure 8 shows the FTIR spectra of different samples of PAni/V_2O_5 hybrids synthesized with the various amounts of aniline as described above. We can take the spectrum of Fig. 8a, corresponding to an aniline:V_2O_5 ratio of 3:1, as a representative example of the first series of hybrids. It presents the characteristic bands corresponding to polyaniline in the emeraldine form (bands in the range from 1000 to 2000 cm^{-1}) as well as bands in the low frequency range assigned to V_2O_5 (512 and 760 cm^{-1} for the V–O–V stretching modes and 1038 cm^{-1} for the V=O stretching). From the series in Fig. 8 we can distinguish three groups of samples (a–c, d–e, f–g) according to the bands at 1600 cm^{-1}.

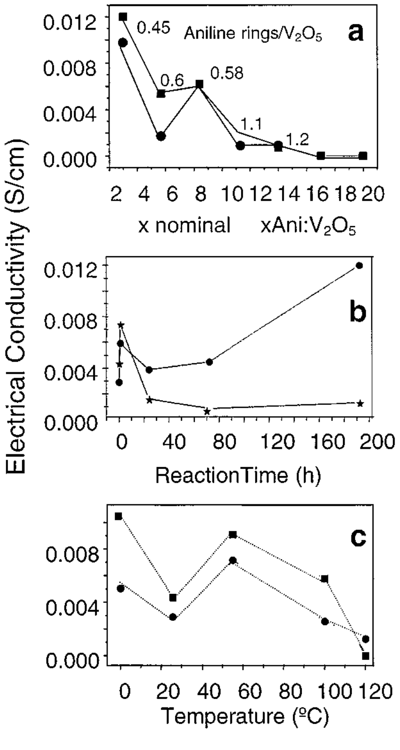


FIG. 5. Electrical conductivity of the hybrids PAni/V_2O_5. (a) Influence of the nominal amount of aniline in the reaction mixture, x (x aniline: 1 V_2O_5). The values indicated correspond to the experimentally found values of x. (b) Influence of reaction times. (c) Influence of reaction temperature. In all cases the measurements were performed immediately after synthesis (●) after 6 days, (■), and after 30 days (★).

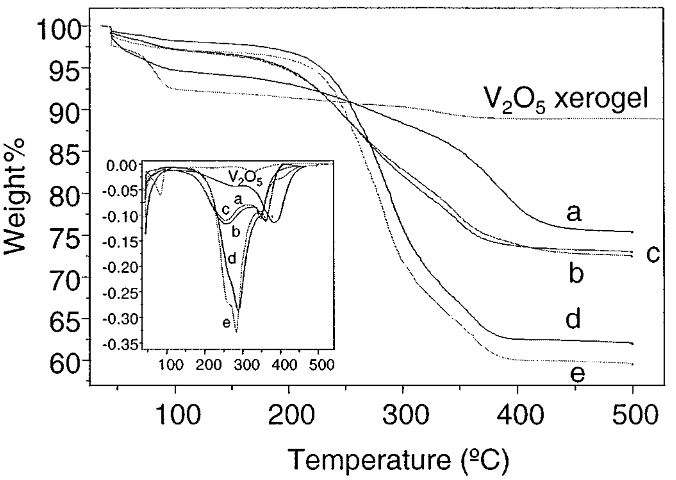


FIG. 6. Thermogravimetric analyses and the corresponding derivative curves d*W*/d*T* (inset) obtained for hybrid PAni/V_2O_5 materials with different nominal Ani/V_2O_5 ratios for V_2O_5. Values of x in x Ani:1 V_2O_5 are (a) 3, (b) 5.7, (c) 8.6, (d) 11.5, and (e) 14.

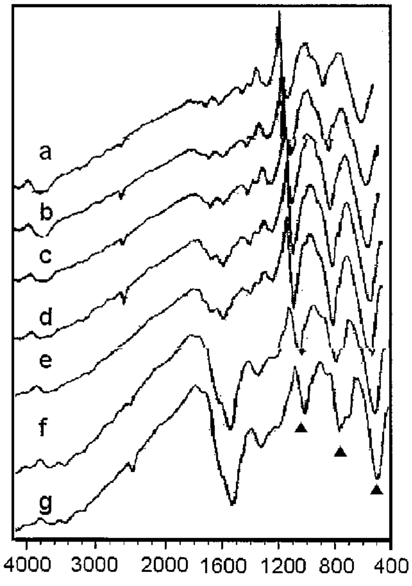


FIG. 8. FTIR spectra corresponding to samples of PAni/V_2O_5 hybrids prepared from reaction mixtures with different aniline: V_2O_5 ratios. Values of x in x Ani:1 V_2O_5 are: (a) 3, (b) 5.7, (c) 8.6, (d) 11.5, (e) 14, (f) 17, and (g) 20. Triangles mark the peaks assigned to V_2O_5.

First of all, a qualitative difference between spectra f–g and the rest is most apparent. This difference must be due to the already mentioned presence of excess aniline in those two samples, probably occluded within the grains of hybrid. On the other hand, there are also less obvious but significant differences between the spectra of samples a–c and d–e. The ratio of intensities of bands at 1550/1470 cm^{-1} is inverted from one group to the other; it is greater than one for samples a–c and smaller than one for samples d–e. This difference comes to support the existence of two phases proposed from the chemical analyses above. However, the strongest support comes from X-ray diffraction data.

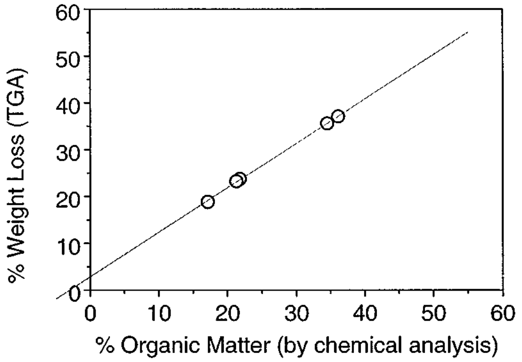


FIG. 7. Plot of percentage weight loss in the range 120–425°C (from TGA) and the percentage of organic matter calculated from chemical analysis. The straight line is a least-squares fit to the five data which are clustered into two groups corresponding to the two phases described in the text.

Powder X ray diffraction patterns for the series of PAni/V_2O_5 hybrids and for the related V_2O_5 xerogel (pattern h) are shown in Fig. 9. The strongest peak at low angles correspond to peak 001 of the layered V_2O_5 structure and is therefore directly related to the interlayer spacing. The main features of the V_2O_5 diffraction pattern (Fig. 9h) are still present in the hybrids, although clearly modified by the appearence of a broad diffuse scattering feature and a decrease in the intensity of peak 001. Then, within the series of hybrids, a clear change in the position of this peak takes place, which marks a difference between samples a–c on the one side and d–g on the other. Samples a–c with aniline/V_2O_5 ratio values of 0.5–0.6 present the 001 peak at 2θ values around 6.5°, which corresponds to interlayer spacings of approximately 14 Å. In the patterns for samples d–g that peak has shifted to lower angles, getting partially obscured by the direct beam tail. Nevertheless, it is possible to determine its position, although with a larger uncertainty, and its location in the range of 4° to 4.5° in 2θ indicates spacings in the range of 23 to 19 Å, substantially larger than for samples a–c.

This behavior is summarized in Fig. 10 and its inset table, which show the evolution of c parameter in relation to the nominal aniline/V_2O_5 ratio used in the preparation of each sample. As happened before with the chemical analysis data, this figure shows two regions with qualitatively different features and confirms the existence of phases with distinct stoichiometries and structures.

The first group of compounds (a–c) present chemical analyses consistent with 0.5–0.6 rings of aniline per V_2O_5 unit and values of c of ca. 14 Å. The second group contain double amounts of polyaniline (ca. 1.2 rings per V_2O_5) and

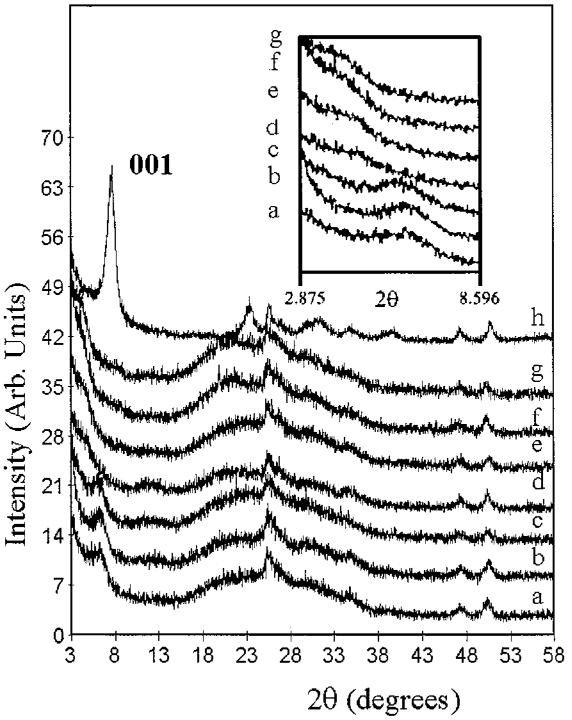
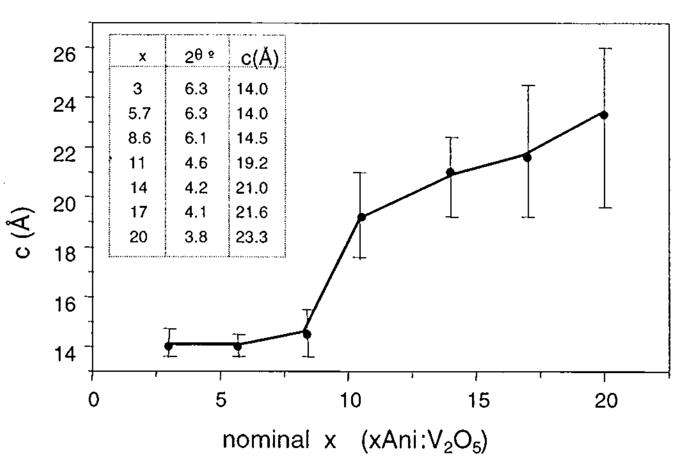


FIG. 9. Powder X-ray diffraction patterns for PAni/V_2O_5 samples synthesized with different aniline/V_2O_5 nominal ratios (x). Values of x in x Ani:1 V_2O_5 are (a) 3:1, (b) 5.7:1, (c) 8.6:1, (d) 11.5:1, (e) 14:1, (f) 17:1, and (g) 20:1. (h) Pattern for a powdered V_2O_5 xerogel prepared from the same hydrogel as the hybrids.

interlayer spacings around 20 Å. Thus, we can conclude that polyaniline intercalation shows two steps leading to the formation of two different phases. The first one represents an expansion from 11.55 to 14 Å. As proposed earlier (6), this difference of about 2.5 Å can be explained by the removal of intercalated water ($\sim$2.8 Å) in V_2O_5 and its substitution by a monolayer of polyaniline (5.3 Å). (6, 23).



x	2θ °	c(Å)
3	6.3	14.0
5.7	6.3	14.0
8.6	6.1	14.5
11	4.6	19.2
14	4.2	21.0
17	4.1	21.6
20	3.8	23.3

FIG. 10. Plot of interlayer spacing in V_2O_5 (c parameter in Å, calculated from the position of 001 peaks) vs nominal aniline/V_2O_5 ratio (x).

On the other hand, the formation of the second phase had not been reported previously. It is associated with an additional expansion of the c parameter to over 20 Å. That represents a total expansion of 9–10 Å from V_2O_5. After considering the 2.8 Å of vacant space left from water removal, the total space which can be assigned to PAni intercalation is of approximately 12 Å. Thus, precisely the samples with double amount of polyaniline per V_2O_5 unit present double space associated to PAni between layers, which makes us conclude that these materials constitute a new PAni/V_2O_5 hybrid phase consisting of a double layer of PAni chains intercalated within the V_2O_5 interlayer spacing.

CONCLUSIONS

The direct synthesis of aniline with bulk V_2O_5 hydrogels has been systematically studied and critical parameters such as reaction temperature and time have been optimized. The reaction takes place with the *in situ* polymerization of aniline within the framework of a previously aged V_2O_5 gel. We have carried out the reaction with different nominal aniline/V_2O_5 ratios and have found out that the materials obtained can be grouped into two phases. The first one, already known, corresponds to the intercalation of a single layer of PAni in the interlayer space and in our materials conforms to the formula $(C_6H_4N)_{0.6}V_2O_5 \cdot XH_2O$, whereas a second novel phase, $(C_6H_4N)_{1.2}V_2O_5 \cdot XH_2O$, incorporates a double layer of polyaniline chains. In addition to the chemical analyses, these two phases can be distinguished by different IR fingerprints and especially by the different interlayer spacings as detected from powder x-ray diffraction patterns. The fact that two distinct phases rather than a continuum of compositions are obtained in this system suggest the existence of a significant interaction between the host and the guest beyond simple insertion into Van der Waals gaps and closer to the formation of true compounds. Given the nature of both components it could presumably involve hydrogen bonding between the organic and the inorganic components. The chemical and electrochemical characteristics of these hybrid materials are heavily dependent upon synthetic conditions. We have been able to get reproducible materials when the synthesis conditions are maintained exactly as described under Experimental.

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