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Iron and arsenic oxide grains are coated with the conducting organic polymer polyaniline. The obtained samples were characterized by infrared spectroscopy, SEM, conducting measurements and thermogravimetry. The thermal stability of both oxides are increased. For As_2O_3 the sublimation temperature is increased from 165°C in the pure oxide to 206°C in the polymer modified sample. The pure Fe_3O_4 sample exhibits sublimation at 780°C whereas the polyaniline coated oxide is stable until at least 1000°C .

Keywords: polyaniline; thermal degradation; oxide.

INTRODUCTION

Polyaniline (PANI) is one of the most studied conducting polymers, not only due the facility in preparation procedures, but also related to high stability to the environmental exposition. The normal polymerization to prepare polyaniline has an enthalpy value of 439 kJ mol^{-1} for the emeraldine form¹, and its protonation (doping)² and many other physical-chemical properties are connected to the presence of the -NH- group³.

A great number of polymers, such as those derivative of polyaniline or other having some electroactive properties can be inserted into inorganic 2D, 3D or porous host solids⁴⁻⁶ as phosphonates⁷⁻⁸, phosphates⁹⁻¹¹, sulfides¹² and oxides¹³⁻¹⁵, displaying the so called nanocomposites¹⁶⁻²¹, which have enhanced their uncommon electrical properties.

Since polyaniline has characteristic photocatalytic properties²², having a conducting band in the visible region which is activated by solar radiation²³, some kind of synergic relationship could arise when PANI is used as part of a organic/inorganic mixed material. In this direction, inorganic matrices such many metal oxides, which exhibit a very wide range of electrical resistivity²⁴ with catalytic²⁵ or photocatalytic properties^{26,27} have been explored. For this purpose, deposition of a layer, or layers of polyaniline on the oxide surface, which polymer is used as a contact interface between oxide and another chemical species and/or electrode surfaces, could exert interesting and important effects on the oxidation-reduction properties of the substrate.

Recently, polyaniline adsorbed on MoO_3 was used to electrocatalyse the oxidation of molybdate ion, enhancing several times the electrode response, and so, can be used as a selective electrode for molybdenum²⁸. The effects of polyaniline on redox process on As_2O_3 were also studied²⁹.

The aim of this work is to study the effects of adsorbed polyaniline on the thermal degradation process for iron and arsenic oxides in an attempting to establish a experimental procedure that allows use this oxides at higher temperatures than the usual ones.

EXPERIMENTAL

Polyaniline was chemically obtained³⁰, by using a 0.50 mol dm^{-3} solution of bidistilled aniline (Aldrich) in 1.0 mol dm^{-3}

HCl (Aldrich) as starting materials. To this solution maintained at 278 K was added, dropwise for 2h, 100 cm^3 of a 0.80 mol dm^{-3} of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. After the complete addition of the oxidant solution, the mixture was stirred for 10 h, until finished the polymerization. The final polymer, was washed several times with distilled water and acetonitrile, to remove oligomers as well another possible impurities. The obtained polyaniline was then treated with a 1.0 mol dm^{-3} of NH_4OH solution to promote deprotonation.

In the next stage, 0.40 g of the prepared polyaniline was dissolved in 45.0 cm^3 of $\text{N,N}'$ dimethylformamide (Merck). This solution was added to 2.0 g of As_2O_3 (99,9%, Carlo Erba) and 0.50 cm^3 of H_3PO_4 to promote the doping². The mixture was aged for 48 h at room temperature, before withdrawing the excess of solution and dried at 363 K overnight. The green powder product containing polyaniline adsorbed on oxide As_2O_3 is named from here as $\text{As}_2\text{O}_3\cdot\text{pani}$. A similar procedure was used to prepare a polyaniline coated Fe_3O_4 sample, producing $\text{Fe}_3\text{O}_4\cdot\text{pani}$.

The pure and polymer coated samples were characterized by FR-IR in a Bomem apparatus, with pressed KBr pellets and 25 scans, TG in a Shimadzu TGA-50 under argon atmosphere with heating rate of $8.3 \times 10^{-2} \text{ Ks}^{-1}$. The SEM images were obtained in a Jeol, JSM T-300 apparatus, using an accelerating voltage of 15 kV . Conductance measurements were taken in a four probe apparatus, using pressed sample discs. No success was achieved in the attempting to obtain ^{13}C CP-MAS spectra for oxide-polyaniline samples.

RESULTS AND DISCUSSION

In comparing the infrared spectra of PANI in Figure 1 with that for As_2O_3 and $\text{As}_2\text{O}_3\cdot\text{pani}$ as shown in Figures 3 (a) and (b), the spectra of $\text{As}_2\text{O}_3\cdot\text{pani}$ shows three bands, which could be assigned as derived from pani bands: at 579 cm^{-1} , 1146 cm^{-1} and 1255 cm^{-1} . In an attempting to assign the last two bands can be associated to those located in free pani at 1140 cm^{-1} and 1301 cm^{-1} , respectively, which are usually attributed to the doping process¹. However, the band at 579 cm^{-1} has not a clear attribution. For Fe_3O_4 and $\text{Fe}_3\text{O}_4\cdot\text{pani}$ samples (Figure 2), a broad peak at 1088 cm^{-1} which could be associated with the free band at 1140 cm^{-1} in free polyaniline is observed. Emeraldine has two types of basic sites capable of coordinating Lewis acids: amine and imine nitrogens. In the polymer chain they are present in equal numbers. As observed for Lewis acid doped polyaniline³¹, both types of sites could be involved in the interaction (coordination) process.

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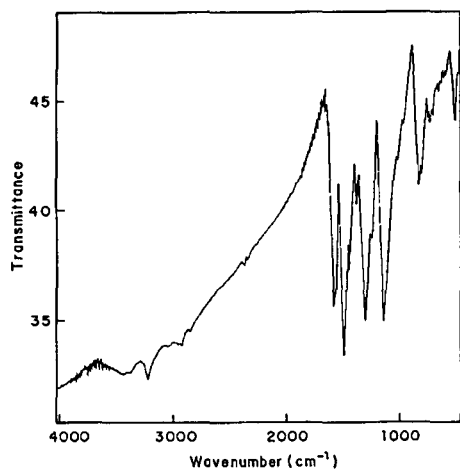


Figure 1. Infrared spectra of polyaniline.

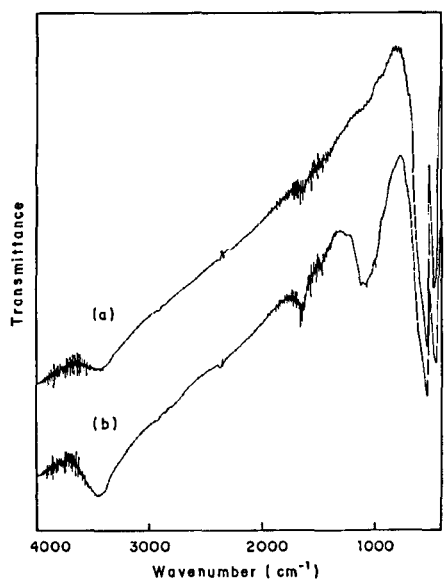


Figure 2. Infrared spectra of (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4.\text{pani}$.

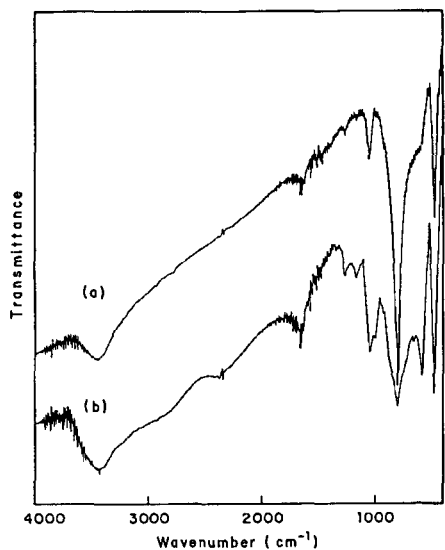


Figure 3. Infrared spectra of (a) As_2O_3 and (b) $\text{As}_2\text{O}_3.\text{pani}$.

The SEM micrographs for the pure and polymer oxide samples are shown in figures 4 and 5. As can be noted, mainly to arsenic oxide, the polymer are adsorbed on the grains surface.

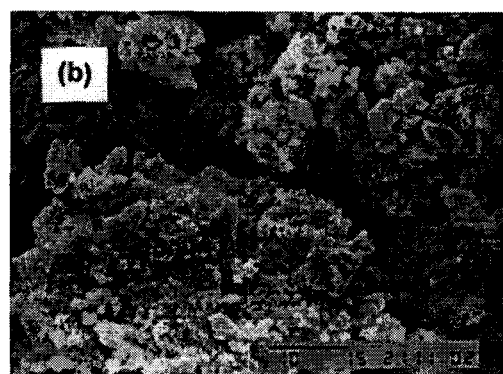
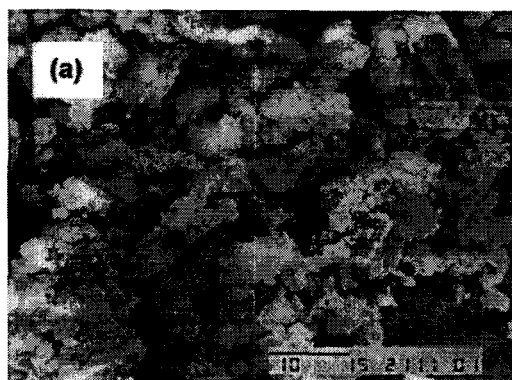


Figure 4. SEM micrographs of (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4.\text{pani}$.

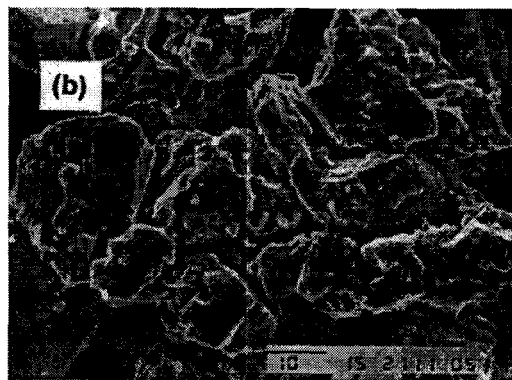


Figure 5. SEM micrographs of (a) As_2O_3 and (b) $\text{As}_2\text{O}_3.\text{pani}$.

The conductivity of pellets obtained by pressing powders are $3.4 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ and $34.2 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$, for As_2O_3 and $\text{As}_2\text{O}_3\text{:pani}$, respectively. These values indicated that the material with polyaniline has a conductivity, which is about ten times larger than that of the pure oxide. This result corroborated that the polymer deposition occurred on the substrate surface.

The thermogravimetric curve of As_2O_3 presents a total mass lost due to the sublimation of the oxide, whereas the TG curve of $\text{As}_2\text{O}_3\text{:pani}$ shows a first mass loss step of 87% due to oxide sublimation and a second one of 13%, due to the thermal degradation of the organic moiety. The second mass loss step exhibits a profile consistent with the thermal degradation of emeraldine³²⁻³³. Thermogravimetric technique can be considered as a reliable tool to characterize solid surfaces^{34,35}, and then, the fraction of 13% can be assumed as been the total amount of deposition of polyaniline on As_2O_3 surface.

For $\text{Fe}_3\text{O}_4\text{:pani}$ a mass loss of 11% can be observed due to the release of polyaniline molecules. So, for both oxides the total amount of adsorbed polyaniline is almost the same.

For both oxides an increase in the thermal stability was observed since the sublimation temperature of arsenic oxide is about 165°C for the pure oxide and 206°C for the polymer modified one. The pure iron oxide sample used sublimes at 780°C whereas the polyaniline modified sample do not sublimate until the maximum temperature used, 1000°C.

The reasons to the observed phenomena could be attributed to the interaction of nitrogen atoms or π electrons of the aromatic rings of polyaniline with the acidic sites in the oxides surfaces, with polyaniline coating sheets acting as a "thermal barrier", since it absorbs the heat transferred to the polymer coated samples.

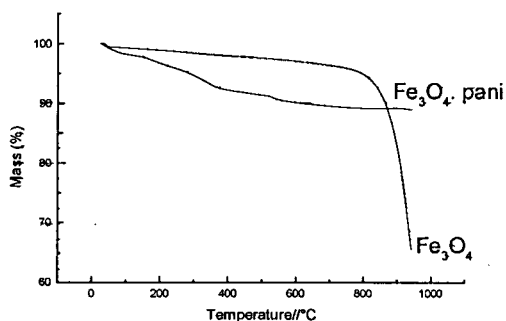


Figure 6. Thermogravimetric curves of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{:pani}$.

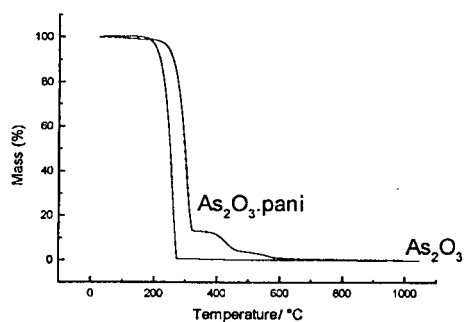


Figure 7. Thermogravimetric curves of As_2O_3 and $\text{As}_2\text{O}_3\text{:pani}$.

CONCLUSION

The obtained experimental results shows that polyaniline can be used to increase the thermal stability of iron and arsenic oxides. Since polyaniline, as well as many metal oxides exhibit

electrical and catalytic properties, an increase in thermal stability could be an desirable improvement in such organic-inorganic materials.

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