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Hybrid Materials Obtained with Iron Oxides

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Abstract: This work describes the synthesis of functionalized iron oxide through surface modification of magnetic iron oxide with tailor-made phenyl-phosphonic acid. Iron oxide were synthesized by precipitation method in "green" conditions, using water as solvent, and by thermal decomposition. The surface modification process was achieved using ultrasonic bath. FT-IR and TGA studies indicate that phenyl-phosphonic acid binds on iron oxides preferably through bidentate bonding mode. They are considered advanced materials, innovative and with promising applications in many areas such as: optical, catalysis, electrical, mechanical, energy, environment, biology or medicine.

Keywords: iron oxide, hybrid materials, phenyl-phosphonic acid, ultrasonic bath, FT-IR, TGA

1. Introduction

The tendency of organophosphonic acids to form monolayers on metal oxide surfaces [1-4] and their significant resistance to homo-condensation and hydrolysis [5,6] make them particularly interesting candidates for such oxidized surface functionalization. The grafting of phosphonic acid compounds was studied on several metal oxides, including iron oxide [7]. Organophosphorus compounds (as phosphate, phosphonate or phosphinate derivatives) offer a promising alternative in the coupling of organic components to metal oxides [8]. The exceptional binding properties of phosphonic acids to oxide surfaces have attracted much attention. Many examples of inorganic nanoparticles (NPs) using phosphonate terminated molecules have recently appeared in the literature (for example the case of gamma-Fe_2O_3 [maghemite] and Fe_3O_4 [magnetite]) [9-12]. This includes also metallic NPs, which are usually surrounded by an oxidized layer. Among inorganic NPs, those based on superparamagnetic iron oxide are intensively studied because of their wide range of applications, including their important use as contrast agents in magnetic resonance imaging (MRI) [13]. Surface-functionalized magnetic nanostructures are especially important because of their potential biomedical applications like in vitro cell separation, in vivo drug delivery, MRI contrast and hyperthermia treatment of cancer cells [14-19]. For in vivo and in vitro applications, the optimized attachment of biomolecules on magnetic nanoparticle surface plays a crucial role in their applicability. To date few studies have dealt with the chemistry area of phosphonic acids binding on the iron oxide surface [23, 24]. This field involves both the coordination of the phosphoryl oxygen to Lewis acid sites and the condensation of P-OH groups with surface hydroxyl groups Fe-OH. The ease of formation and stability of M(Fe)–O–P bond is well described in literature [25]. The surface modification of some transitional metal oxides with bi-functional organo-phosphorous coupling agents is also studied. Surface modification of magnetic iron oxides by alkyl phosphonates have also been studied by some researchers [20-22,26,27]. The surface modification of Fe_2O_3 particles with phosphonic acids $RPO(OH)_2$ is currently attracting increasing interest for numerous applications.

2. Experimental

2.1. Materials

The reagents: phenyl-phosphonic acid (PPA) $C_6H_5P(O)(OH)_2$ (Fluka), vinyl-phosphonic acid (VPA) $C_2H_5PO_3$ (Merk), etidronic acid $C_2H_8O_7P_2$ (Sigma Aldrich), undecenyl-phosphonic acid (SP-61-003) $CH_2{=}CH[CH_2]_9PO(OH)_{2b}$ (CédricLombard) (Specific Polymers- http://www.specificpolymers.fr/), silica mesostructured (MCM-41 type-Mobil Composition of Matter No. 41) (Sigma Aldrich), controlled pore glass, CPG75C, 75 angstrom, 37-74 µm, 20 GM (Millipore), iron(III) acetylacetonate and water were used as purchased.

2.2. Methods

Jasco FT-IR 4200 Spectrometer, KBr support was used for recording the spectra.

Thermal analysis TG-DTG-DTA (Thermogravimetry or TGA) was carried out by changing the temperature between 20°C and 900°C, by using a 851-LF 1100-Mettler Toledo apparatus in air flow. It has a sensibility of 1 µg. The maximum amount of the sample wich could be measured is 5 g.

EDX characterizations were made using a Jeol JSM 6400 X- ray microanalizor EXL II System Link Analytical with a detector of 133 eV.

Grafting of phenyl phosphonic acid on nanocomposites containing iron oxide

In a flask Berzelius 0.5 g nanocomposites containing iron oxide were dispersed in 50 ml water. Then this mixture was added dropwise to a solution which contained 0.55 g phenyl-phosphonic acid (PPA) in 50 ml water, over 20-30 minutes. The reaction mass in the flask was allowed under stirring for 15-20 hours. At the end of the synthesis, the reaction mixture was filtered in vacuo, resulting in a precipitate. The synthesized compounds were left to dry for 3 days in niche, to dryness (C1@PPA, C2@PPA, C3@PPA).

Grafted iron oxides with phosphonic acids in ultrasonic bath

In a Berzelius flask containing 50 mL water, 0.5 g iron oxide nanoparticles obtained by precipitation method, were dispersed. Then the corresponding amount of the phosphonic compound dissolved in 50 mL water was added dropwise to the mixture (0.55 g phenyl-phosphonic acid resulting the compound C4; 0.4g vinyl-phosphonic acid resulting the compound C5; 0.7 g etidronic acid resulting the compound C6; 0.003 g SP-61-003 undecenyl phosphonic acid resulting the compound C7). The reaction was carried out in the ultrasonic bath, over a period of time of 15-20 minutes. The resulting mixture was left under stirring for 12-15 hours. Passed this time, the reaction mixture was filtered through a fluted filter, resulting in a dark brown precipitate, while the filtrate is clear. The precipitate was dried 3 days at room temperature.

3. Results and Discussion

The FT-IR spectrum for synthesized materials (Figure 1), showed intense absorption bands that proved the grafting of phosphonic acid onto the Fe_2O_3, at: $\nu_{(P=O)}$ = 1147.44 cm^{-1}, $\nu_{(P-C)}$ = 1333.53 cm^{-1}, $\nu_{(C-H)}$ = 3052.76 cm^{-1}.

Based on this spectrum, we can clearly see the presence of an important band overlapping in the 888.059-1637.91 cm^{-1} regions corresponding to the different vibration modes of the phosphonic acid confirming the grafting of the molecules on the surface. Unfortunately, the absorption bands in this region are too poorly defined to clearly identify them and eventually determine the way the bifunctional molecules bind to the surface. In this spectrum, very weak C–H asymmetric and symmetric stretching vibration bands can also be observed around 3052 cm^{-1}. The bands in the regions of 888.059 cm^{-1}, 1147.44 cm^{-1} and 1637 cm^{-1}, were attributed to stretching and vibrations of the Fe–O–Fe group, and the one at 3741.23 cm^{-1} was attributed to Fe–O–P indicating the grafting of the phosphonic acid on the Fe_2O_3. The band ascribed to superficial Fe–O vibrations appeared at 692.32 cm^{-1}. The FT-IR spectrum also shows a band at: $\nu_{(P-O)}$ = 1033.66 cm^{-1}. These values are indicatives of weakly organized monolayers. Based on all these results we can confirm the grafting of the phosphonic acid on the Fe_2O_3 (Fig.1). The TGA spectra (Fig.2) showed that compounds C5, respectively C7, are more stable (do not lose mass). The compound C7 it is the most stable and it loses very little mass, about 0.1% , while the compound C5 loses about 3.68%. The compound C5 lost up to 200^0C about 2.54% H_2O, and in the range 226–367^0C about 1.14% vinyl-phosphonic acid.

The compound C6 is unstable and it loses mass continuous up to 155 ^{0}C, about 15.8 %, after which the rate of decomposition decreases and at the temperature of 317 ^{0}C it loses about 3.6% H_2O. From temperature 340^0C, it is possible to form new links Me–O. On TG curve it registers a growth from mass of about 0.38 % up to temperature 395 ^{0}C.

4. Conclusions

The grafting of the surface of iron oxide particles, under “green” conditions, was investigated by FT-IR and TGA. The compounds synthesized in the present work are new materials. Moreover, in our work, the ultrasonic bath was used for the first time for obtaining such materials. After TGA analysis it was proved that the process of grafting takes place with a higher yield for the compounds that break down easier. Based on FT-IR analysis, the grafting of phosphonic acid on Fe_2O_3 was confirmed.

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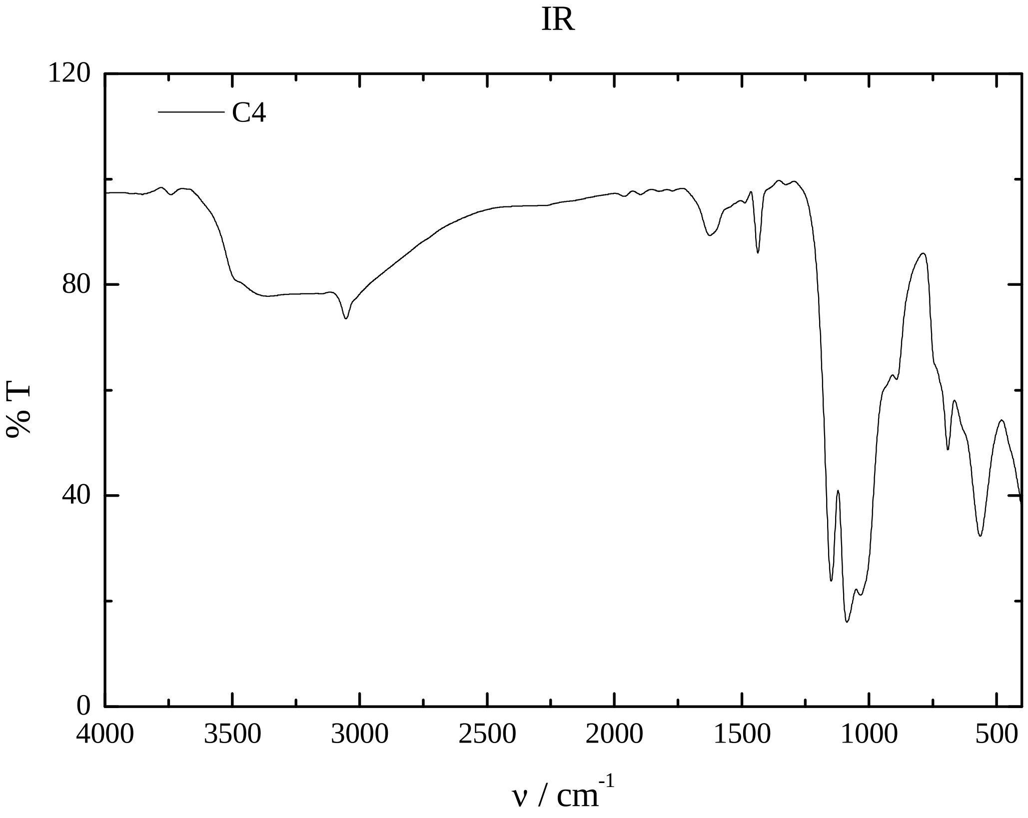

Figure 1. The characteristic FT-IR spectrum for class of synthesized graftingof acid phenyl phosphonic the Fe_2O_3 (C4)

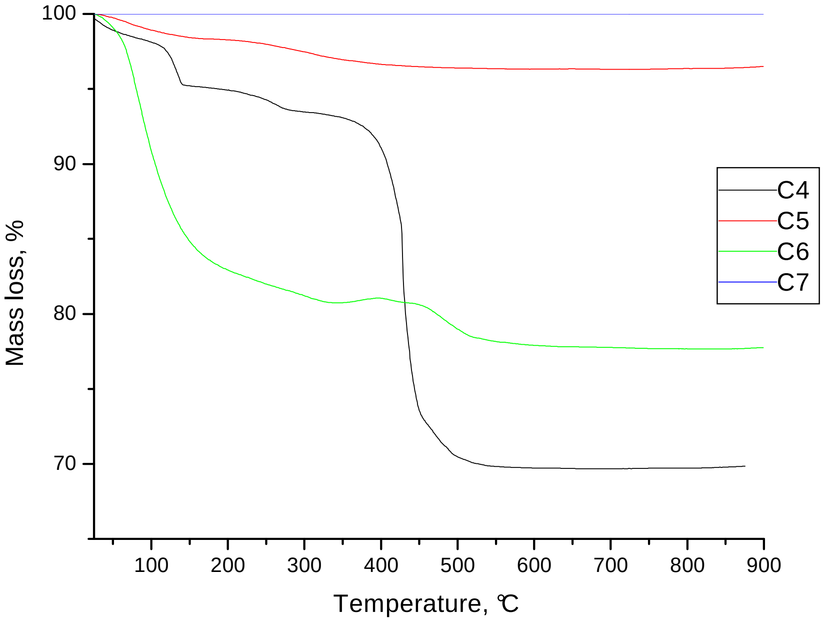

Figure 2. TGA spectra of C4-C7 compounds

REFERENCES

1. Folkers J.P., Gorman C.B., Laibinis P.E., Buchholz S., Whitesides G.M. and Nuzzo R.G., *Langmuir*, 11, **1995**, 813–824.
2. Gao W., Dickinson L., Grozinger C., Morin F.G. and Reven L., *Langmuir*, 12, **1996**, 6429–6435.
3. van Alsten J.G., *Langmuir*, 15, **1999**, 7605–7614.
5. Quiñones R., Raman A. and Gawalt E.S., *Surface Interface Analysis*, 39, **2007**, 593–600.
6. Mutin P.H., Guerrero G. and Vioux A., *Comptes Rendus Chim.*, 6, **2003**, 1153–1164.
7. Fadeev A.Y., *Langmuir*, 20, **2004**, 2270–2273.
8. Paszternak A., Stichleutner S., Felhosi I., Keresztes Z., Nagy F., Kuzmann E., Vertes A., Homonnay Z., Peto G. and Kalman E, *Electrochim. Acta*, 53, **2007,** 337–345.
9. Nakatsuka T., Kawasaki H., Katsuhiko I. and Yamashita S.J., *Appl. Polym. Sci.*, 27, **1982**, 259-264.
10. White M.A., Johnson J.A., Koberstein J.T. and Turro N.J.J., Am. Chem. Soc., 128, 2006, 11356-11357.
11. Yee C., Kataby G., Ulman A., Prozorov T., White H., King A., Rafailovich M., Sokolov J. and Gedanken A., *Langmuir*, 1, **1999**, 7111-7115.
12. Chouhan G., Wang D.S. and Alper H., *Chem. Commun.*, 45, **2007**, 4809-4811.
13. Hu A.G., Yee G.T. and Lin W.B.J., *Am. Chem. Soc.*, 127, **2005**, 12486-12487.
14. Laurent S., Forge D., Port M., Roch A., Robic C., Elst L.V. and Muller R.N., *Chem. Rev.*, 108, **2008**, 2064-2110..
15. Gupta A.K. and Curtis A.S.G., *J. Mater. Sci. Mater. Med.*, 15, **2004**, 493–496.
16. Hergt R., Hiergeist R., Hilger I., Kaiser W.A., Lapatnikov Y., Margel S. and Richter U., *J. Magn. Magn. Mater.*, 270, **2004**, 345–357.
17. Johannsen M., Jordan A., Scholz R., Koch M., Lein M., Deger S., Roigas J., Jung K. and Loening S., *J. Endourol.*, 18, **2004**, 495–500.
18. Kodama R.H., *J. Magn. Mater.*, 200, **1999**, 359–372.
19. Li G.X., Joshi V., White R.L, Wang S.X., Kemp J.T., Webb C., Davis R.W. and Sun S.H., *J. Appl. Phys.*, 93, **2003**, 7557–7560.
20. Gupta A.K. and Gupta M., *Biomaterials*, 26, **2005**, 3992–4021.
21. Bruce I.J. and Sen T., *Langmuir*, 21, **2005**, 7029–7035.
22. Yee C., Kataby G., Ulman A., Prozorov T., White H., King A., Rafailovich M., Sokolov J. and Gedanken A., *Langmuir*, 15, **1999**, 7111–7115.
23. Sahoo Y., Pizem H., Fried T., Golodnitsky D., Burstein L., Sukenik C.N. and Markovich G., *Langmuir*, 17, **2001**, 7907–7911.
24. Gao W., Dickinson L., Grozinger C., Morin F.G. and Reven L., *Langmuir*, 12, **1996**, 6429-6435.
25. Randon J., Blanc P. and Paterson R.J., *Membr. Sci.,* 98, **1995**, 119-129.
26. Clearfield A., *Curr. Opin Solid State Mater.*, 6, **2002**, 495–506.
27. Holland G.P., Sharma R., Agola J.O., Amin S., Solomon V.C., Singh P., Buttry D.A. and Yarger J.L., *Chem. Mater.*, 10, **2007**, 2519–2526.
28. Portet D., Denizot B., Rump E., Lejeune J. and Jallet P., *J. Colloid Interface Sci.*, 238, 2001, 37-42.

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