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MAGNETIC PROPERTIES OF SMALL AMOUNT OF Fe_2O_3 IN SILICA-POLYVINYL ALCOHOL MATRICES NANOCOMPOSITES

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Abstract
^{1}H and ^{29}Si MAS NMR, and Mössbauer spectroscopy of a prepared series of sol–gel Fe_2O_3-silica/PVA nanocomposites materials containing 0.1; 1; 2; 5; and 10% Fe_2O_3 are reported. The ^{29}Si NMR typically shows three Q-species ($Q^{2,3,4}$) in the initial gels, and as heat treatment temperature is increasing the average n of the Q^n-species increases as well. The observed behaviour can be attributed to the organic fragments and hydroxyl groups removal. The proton spectra reflect the proton-content decrease as the temperature of the heat treatment increases. For certain temperatures the grow and the stability of some phases are influenced by differential thermal treatment as the Mössbauer spectroscopy revealed.
Keywords: iron oxide, ^{1}H MAS NMR, ^{29}Si MAS NMR, Mössbauer spectroscopy.

1. Introduction

The use of an inorganic matrix as a host for nanocrystalline particles can provide an effective way for tailoring a particle-size distribution as well as controlling the homogeneous dispersion of metal oxide particles [1]. Magnetic iron oxide nanoparticles exhibit enhanced surface effects, superparamagnetic behaviour [2]. Iron oxide nanoparticle applications are many and diverse; as magnetic recording media [3], in optics [3], in ferrofluids [3], in catalysis [1] and in biology [1]. In addition, sol–gel methods have been found effective for creating dispersions of small magnetic particles in inorganic matrices [4].

In this study the sol-gel synthesis and characterisation of some iron oxide embedded on SiO_2-PVA matrices was carried out. The aim of the present study was identification of the iron oxide phases with the increased temperatures. The obtained xerogels and thermal treated samples were characterised by ^{1}H, ^{29}Si MAS NMR and Mössbauer spectroscopy .

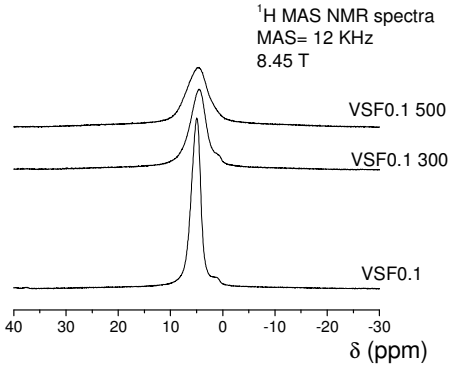
2. Method and samples

In the present work, transparent Fe_2O_3-SiO_2/PVA sol-gel derived monoliths were obtained. Tetraethoxysilane (Sigma-Aldrich, 98%), polyvinyl alcohol (M=13,000-23,000

g/mol (Sigma-Aldrich, p.a.) and iron nitrate (Sigma-Aldrich, p.a.) were used. TEOS was dissolved in half amount of ethanol. Iron nitrate was dissolved in another amount of ethanol. PVA was pre-dissolved in hot water to obtain 2% of PVA in silica matrix. Then, the TEOS ethanolic solution was added to iron nitrate solution and after to PVA and water mixture. The homogeneous, clear sol was stirred for 2 hours. The ratio TEOS/EtOH/H_2O was 1:3.85:10. The xerogels were calcined at different temperatures: 300°C, 500°C, 700°C, 900°C and 1000°C for 2 hours using 2°C/min. The ^{1}H NMR spectra were recorded using a Varian-Chemagnetics CMX 360 (8.45 T) spectrometer operating at 360.13 MHz, using a 1-pulse sequence with a 4 μs pulse (~90°) and a 20 s recycle delay, with 128 acquisitions added together. The chemical shift was referenced externally to adamantane at 1.8 ppm. ^{29}Si MAS NMR spectra were collected on a Bruker MSL 300 spectrometer (7.05T) operating at 59.62 MHz. A 1.5 ms pulse (~30°) was used with a 20 s recycle delay. ^{29}Si spectra were referenced to TMS at 0 ppm. Mössbauer spectra were carried out at room temperature. Measurements were done in transmission mode with ^{57}Co diffused into a Cr matrix as a source moving with constant acceleration.

3. Results and Discussions

^{1}H MAS NMR spectra are shown in Fig. 1 for VSF0.01 sample. As can be seen from xerogel spectra a broader peak appears around 7 ppm which can be attributed to the external hydrogen bounded silanols within the samples [5].



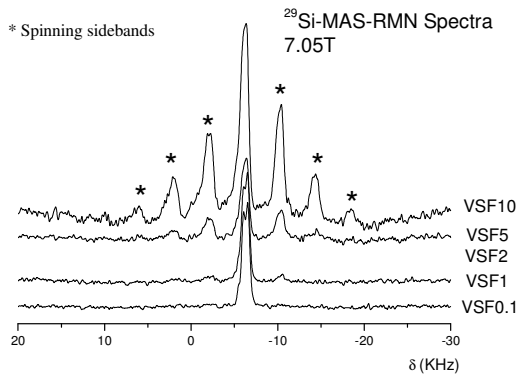


Fig. 1. ^{1}H MAS NMR Spectra of VSF0.1, xerogel and thermal treated at 300 and 500°C	*Fig. 2. ^{29}Si-MAS-NMR Spectra of Fe_2O_3 in hybrid matrix*

The resonance of water appears between 2-4 ppm as a very broad peak. As the temperature of calcinations as is increased the signal of the protons from ^{1}H MAS NMR

spectra decrease. This means that the hydroxyls were partially eliminated from the surface by calcination.

^{29}Si MAS NMR spectra of iron oxide-silica/PVA are presented in figure 2. In the spectra of iron oxide in silica matrices appear spinning sidebands whose concentration increase with increasing of iron oxide concentration. Simulations of the spectra were carried out using dmfit software [6] with three Gaussian contributions corresponding to Q^2, Q^3 and Q^4 species. It was observed an increase in the higher n Q^n species (especially Q^4) with increasing heat treatment temperature. Heat treatment to progressively higher temperatures leads to the loss of organic groups and to further condensation which strengthens the silica network and eventually leads to the presence of only Q^4 species (i.e. virtually all of the tetrahedra are connected SiO_4 to four other units).

The Mössbauer spectrum for VSF10 1000 sample is presented in Fig. 3.

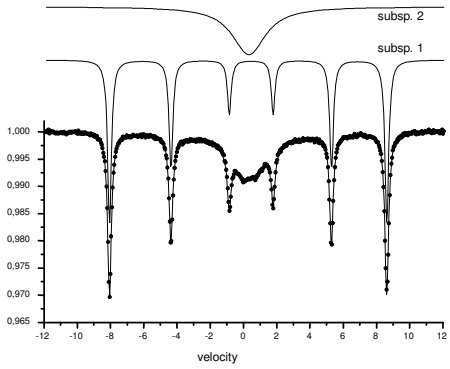


Fig. 3. Mössbauer spectrum of VSF10 1000 sample

The hyperfine parameters of Mössbauer spectrum and the evaluation of are magnetic phase content presented in the tables 1 and 2.

Table 1. Spectral parameters of Mössbauer spectra for VSF10 1000 sample

	Izomer shift δ	Quadrupole splitting ΔEQ	Hyperfine field, BHf	Relative intensity (%)	Assignment
Subsp. 1	0,37 mm/s	- 0,18 mm/s	51,8 T	60	α-Fe_2O_3 - hematite
Subsp. 2	0,33 mm/s	0,01 mm/s	47,0 T	40	para (superpara)

The fitting of the spectra was performed with the help of the NORMOS program.

Table 2. Magnetic phase content of measured samples

Sample	Annealing T	Magnetic behavior at room temperature	Concentration [%]
VSF2 1000	1000 °C	Paramagnetic	100 α-Fe_2O_3
VSF5 1000	1000	Paramagnetic	100 α-Fe_2O_3
VSF10 700	700	Paramagnetic	100 α-Fe_2O_3
VSF10 900	900	Paramagnetic	100 α-Fe_2O_3
VSF10 1000	1000	Ferimagnetic	50% ε-Fe_2O_3
		Paramagnetic	50% α-Fe_2O_3

4. Conclusions

The variation of intensity of the ^{1}H MAS NMR spectra reflects that, as the temperature of the heat treatment increases, the proton-content decreases. As ^{29}Si MAS NMR spectra revealed the resulting increase in the cross-linking of the network leads to an increase in the proportions of higher n Q^n species. Mössbauer spectra revealed that depending of the temperature and the concentration of iron oxide in hybrid matrix are obtained different phases and concentrations in silica matrices.

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