Structural changes induced in nanostructured silica core - alumina shell microspheres doped with iron and gadolinium investigated by solid-state NMR Spectroscopy

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Abstract

We report new nanostructured silica core-alumina shell microspheres doped with paramagnetic ions, obtained by a chemical synthesis based on Stöber method for the silica core, and electrostatic attraction for nucleation of shell [1]. Amorphous character of the structures was highlighted by XRD. Structural changes that occur in samples by changing the concentration of paramagnetic ions from the shell are studied by solid-state NMR. Shape and size of microspheres were investigated by TEM. The results show that the paramagnetic ions have a disordering effect, partially substituting aluminium, which was incorporated in silica network. We have obtained stable amorphous microspheres with highly porous shell, and paramagnetic ions on the outermost layer of the structures, having potential application as contrast agents in magnetic resonance imaging.

1. Chemical synthesis

Systems: $SiO_2 \cdot (100 - x)\, Al_2O_3 \cdot x Gd_2O_3$ and $SiO_2 \cdot (100 - x)\, Al_2O_3 \cdot x Fe_2O_3$, with x = 0, 5, and 10 % mol

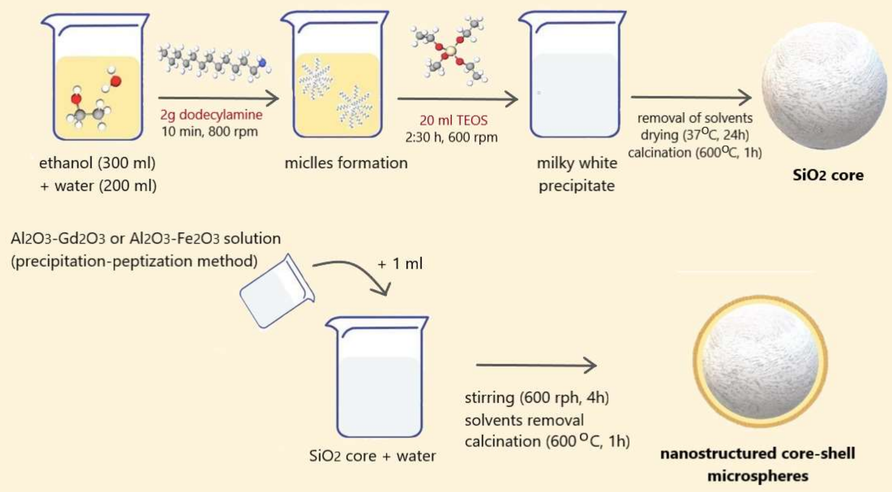

Fig. 1 *Chemical synthesis of core-shell aluminosilicate microspheres doped with different concentrations of gadolinium or iron ions*

2. X-ray diffraction

X-ray powder patterns show a broad diffraction peak between 10° and 40° with a maximum of 2θ at 23°, which points out an amorphous structure of the samples

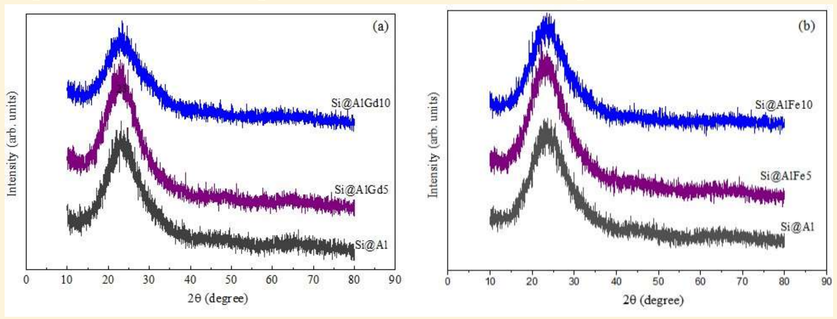

Fig. 2 X-ray diffraction of Si@AlGdx (a) and Si@AlFex (b) structures for Gd or Fe = 0, 5, 10 % mol

3. ^{29}Si and ^{29}Si CP MAS NMR

^{29}Si MAS-NMR spectra of all the samples have a broad resonance line characteristic for amorphous phases with contributions from Q^3 and Q^4 units. A part of aluminum atoms is incorporated in silica network from outermost core layers.

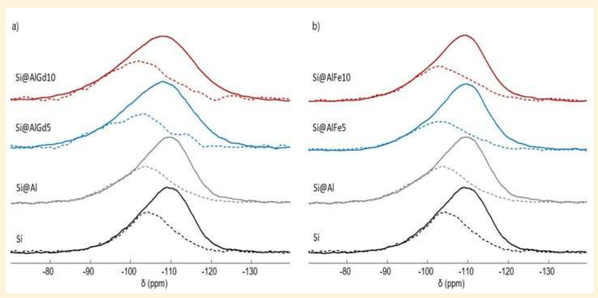

Fig. 3 *^{29}Si (continuous lines) and ^{29}Si CP MAS (dotted lines) NMR spectra*

Table 1 *The chemical shift (δ), line width (FWHM) and fraction of Q^n units (fQ^n).*

Sample	Q^n	δ (ppm)	FWHM (ppm)	fQ^n (%)
Si	Q^3	-104.2	13.4	47.7
	Q^4	-111.2	10	52.3
Si@Al	Q^3	-102.9	14.6	41.9
	Q^4	-110.5	10.3	58.1
Si@AlGd5	Q^3	-101.2	19.9	45.2
	Q^4	-109.8	14.4	54.8
Si@AlGd10	Q^3	-100	19.6	39.9
	Q^4	-109.7	15.8	60.7
Si@AlFe5	Q^3	-101.5	12.8	28.9
	Q^4	-110.2	11.4	71.1
Si@AlFe10	Q^3	-101.9	14.1	37.6
	Q^4	-110.2	11.1	62.4

4. ^{27}Al triple-quantum (3Q) and ^{27}Al MAS NMR Spectroscopies

Three different phases are observed, one corresponding to 4-fold aluminum and two corresponding to 6-fold aluminum.

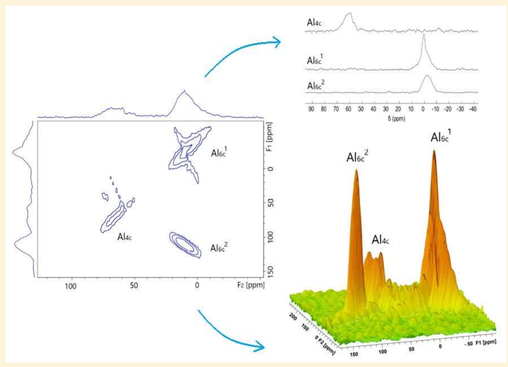

Fig. 4 *^{27}Al 3Q MAS NMR spectra of AlGd0.5 shell*

Table 2 *NMR parameters of simulated Al_{nc} lines from ^{27}Al MAS NMR spectra of samples. δ is the isotropic chemical shift, Cq is the quadrupole coupling constant and fAl_{nc} is the fraction of differently coordinated aluminum, Al_{nc}.*

Sample	Al_{nc}	δ (ppm)	Cq (MHz)	fAl_{nc} (%)
Si@Al	Al_{4c}	57.4	2.7	66.5
	Al_{6c}^1	0.1	0.6	5.1
	Al_{6c}^2	0.7	8.2	28.4
Si@AlGd5	Al_{4c}	56.6	3.5	56.9
	Al_{6c}^1	11.6	3.1	14.7
	Al_{6c}^2	6.9	8.7	28.4
Si@AlGd10	Al_{4c}	54.3	3.7	53.7
	Al_{6c}^1	8.9	4.3	34.3
	Al_{6c}^2	3.7	8.9	12
Si@AlFe5	Al_{4c}	57.3	3.0	68.4
	Al_{6c}^1	0.81	0.7	10.7
	Al_{6c}^2	-3.03	8.4	20.9
Si@AlFe10	Al_{4c}	57.5	3.1	69.3
	Al_{6c}^1	0.85	0.7	10.6
	Al_{6c}^2	-3.6	8.6	20.1

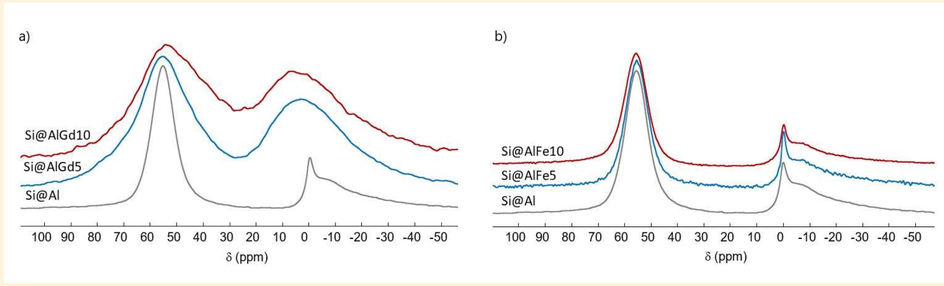

Fig. 5 *^{27}Al MAS NMR spectra* of Si@AlGdx (a) and Si@AlFex (b) structures for Gd or Fe = 0, 5, 10 % mol

With the increase of the gadolinium concentration, the signals become larger, indicating a higher local structure disorder. However, paramagnetic effects must be taken into account.

5. TEM microscopy

Well-defined spherical particles with a mean diameter less than 1.5 μm were obtained. Core-shell structure formation is shown for Si@Al which has a rough surface.

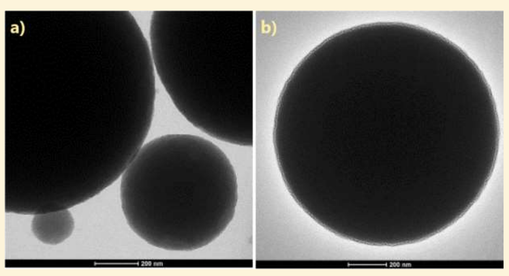

Fig. 6 *TEM micrographs of Si (a) and (c) Si@Al (scale bar 200 nm) nanostructured microspheres*

Conclusions: NMR results evidence the presence of Q^3 and Q^4 units, with preponderance of the last ones, indicating a high network connectivity of the structural units represented by SiO_4 tetrahedra inside the core. Gadolinium and iron have a local structure disordering effect beside their paramagnetic effect. Stable amorphous microspheres with gadolinium ions or iron on the outermost layer of structures were obtained, being promising materials that can be used as contrast agents in MRI.

References

[1] M. Todea *et all.,* J. of Sol-Gel Sci. and Techn., 2020, 96(2), DOI: 10.1007/s10971-020-05346-4

Acknowledgements

A.S. gratefully acknowledge the financial support from Babes Bolyai University in the form of a research fellowship, grant no. 35738/09.12.2020