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SOL-GEL MONOCOMPONENT NANO-SIZED OXIDE POWDERS*

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Sol-gel processes allow synthesis of powders with a more elaborate structure from point view of composition, purity, size and size distribution. In the powders case, sol-gel refers to processing in a liquid medium to obtain a solid matter which does not settle under gravity - that is to say which does not precipitate. In water presence, the precursors undertake the following succession of transformations: hydrolysis → polymerization → nucleation → growth. Sol-gel monocomponent powders have been obtained in Al_2O_3, TiO_2, MgO, Fe_2O_3 system and have been characterized by X-ray diffraction (XRD), IR-spectroscopy, DTA/TGA analysis, transmission electron microscopy (TEM) and BET specific surface area methods. In the used experimental conditions amorphous, nano-sized and monodisperse powders have been obtained. The great value of specific surface area and the great tendency of crystallisation underlines the high reactivity of this powders. Such powders may be used as raw materials for advanced polycrystalline ceramics preparation, as pigments, catalysts or support in chromatography.

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Keywords: Nano-sized powders, Sol-gel method

1. Introduction

The design of advanced ceramics depends on the availability of powders with outstanding properties in terms of composition, purity, size, and size distribution. Sol-gel processes allow synthesis powders to have a more elaborate structure. In the powders case, sol-gel refers to processing in a liquid medium to obtain a solid matter (sol or gel) which does not settle under gravity - that is to say which does not precipitate. The first occurrence of solid particles in solution can be described by a succession of chemical reactions, from an initial chemical compound of a cation M, called the precursor. These solid particles are called primary particles. In water presence, the precursors undertake the following succession of transformations: hydrolysis → polymerization → nucleation → growth [1]. Hydrolysis consists of binding some molecular groups containing oxygen atoms O to a metal M, while polymerization consists in bridging two or more cations M with these ligands. In the case of nonionized precursors such as the alkoxides $M(OR)_n$ these reactions are presented down:

$$M(OR)_n + xH_2O \rightarrow M(OH)_n(OR)_{n-x} + xROH \tag{1}$$

$$-M\text{-}OH + HO\text{-}M- \rightarrow -M\text{-}O\text{-}M- + H_2O \tag{2}$$

The evolution can be such as to produce directly a very open monolithic structure, a polymeric macromolecule called polymeric gel. Linear polymeric structures are enhanced when hydrolysis is slow compared to polymerization. With alkoxides, the precursor concentration and the water concentration for hydrolysis can be controlled by dissolution in a solvent which is often the

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parent alcohol to the precursor. The obtaining of monosized powders can also be achieved with a number of oxides. A typical standard deviation for their size distribution is of the order of 15 % [1].

The advantages of sol-gel powders comparative with conventional powders are:

- the small average particle size and narrow size distribution, in which case they can be called monodispersed;
- homogeneity at molecular level;
- purity and increased reactivity (which determine low processing temperature);
- possibility to obtain nano-sized powders.

For practical applications, these advantages must to exceed the disadvantages of increased cost, of long processing time and of low efficiency.

Such powders may be used as raw materials for advanced polycrystalline ceramics preparation [2-4], as pigments, catalysts or support in chromatography.

In the present work, the sol-gel processing and characterization of the powders in Al_2O_3, TiO_2, MgO, Fe_2O_3 monocomponent systems are presented.

2. Experimental

The compositions of the starting solutions and the experimental conditions used for nano-sized sol-gel monocomponent oxide powders Al_2O_3, TiO_2, MgO, Fe_2O_3 are listed in Table 1.

Table 1. Composition of starting solutions and experimental conditions for nano-sized sol-gel monocomponent oxidic powders Al_2O_3, TiO_2, MgO, Fe_2O_3 preparation.

Sample	Molar ratio			pH	Conditions of reaction	
	$\frac{R-OH}{M(OR)_n}$	$\frac{H_2O}{M(OR)_n}$	$\frac{NH_4OH}{M(OR)_n}$		T (°C)	t (h)
Al_2O_3[a]	-	100	-	6.5	80	1
TiO_2[b]	85*	5	-	5.5	25	0.5
MgO_2[c]	17**	6.1	0.4	10	70	1.5
Fe_2O_3[d]	51.5*	33.1	11.6	~11	70	24

[a] $M(OR)_n = Al(O\text{-}iC_3H_7)_3$
[b] $M(OR)_n = Ti(O\text{-}C_2H_5)_4$
[c] $M(OR)_n = Mg(O\text{-}C_2H_5)_2$
[d] $M(OR)_n = Fe(acac)_3$
* $R\text{-}OH=C_2H_5OH$
** $R\text{-}OH=CH_3OH$

The hydrolysis of aluminium and titanium alkoxides took place in uncatalysed reaction mixture [5, 6]. Base catalysis was used for preparation of magnesium and iron powders after proper procedure. The hydrolysis of aluminum and iron alkoxides took place with a high water excess due to the lower evolution of their hydrolyse-polycondensation reactions. The increased reactivity of titanium alkoxide justified the development of reaction at room temperature for this case. The MgO and Fe_2O_3 sol-gel powders have been prepared also by Lopez et al. [7] and Yogo et al. [8].

Sol-gel monocomponent powders were characterized by X-ray diffraction (XRD), IR-spectroscopy, DTA/TGA analysis, transmission electron microscopy (TEM) and BET specific surface area methods.

3. Results

It is well known that powders obtained by sol-gel method contain always adsorbed and structural water, as well as organic residues. The evolution of the mentioned components at different temperatures, obtained by DTA/TGA is presented in Fig. 1. In all cases the endothermal effects in the

20-160 °C temperature range are assigned to the evolution of adsorbed water and alcohol and in the range of 150-400 °C to the removal of residual OH groups. The water elimination in the case of aluminium oxide takes place in two steps, the second one being accompanied by the endothermal effect at 460 °C. The thermal behaviour of aluminium oxide powder is characteristic to pseudo-boehmite decomposition. The exothermic effect, without mass loss, at about 675 °C, noticed in the DTA/TGA curve of TiO_2 powder is assigned to the anatase → rutile transformation.

For Mg containing powder, the $Mg(OH)_2$ decomposition is emphasized by strong endothermal effect at 405 °C, with a significant mass loss simultaneously with MgO crystallisation.

The exothermic effect at about 542 °C for the iron containing powder points out the crystallisation of α-Fe_2O_3.

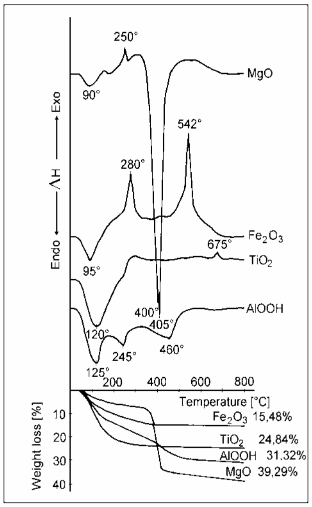

Fig. 1. DTA/TGA results for all samples studied.

The IR spectra of the initial oxide powders, as well as those of the thermally treated samples, for removal of water and organic groups (at 450 °C for AlO(OH), MgO, Fe_2O_3 and 300 °C for TiO_2 sample), are presented in Figs. 2 and 3.

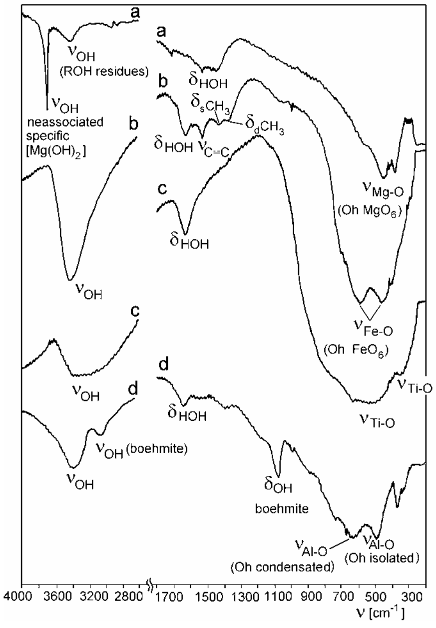

Fig. 2. IR spectra of initial oxide powders.

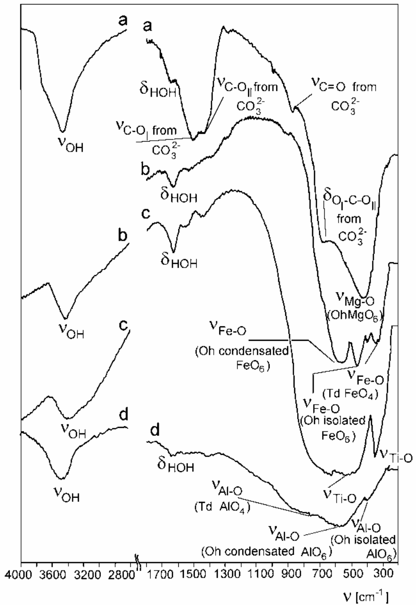

Fig. 3. IR spectra of thermally treated samples [at 450 °C for AlO(OH), MgO, Fe_2O_3 and 300 °C for TiO_2 sample].

In all cases the characteristic vibrations due to the presence of molecular water (3440 cm^{-1}) and structural OH^- (1640 cm^{-1}), as well as those due to M-O-M bonds (800 - 300 cm^{-1}) are observed. After the low temperature thermal treatment, mentioned above, the IR vibrations due to the molecular water and structural OH^- decrease and the vibrations due to M-O-M bonds increase and are better defined. Some changes in the position of the IR bands in the M-O-M region are noticed, that could be assigned to the nanocrystallization of the oxides. The IR spectra have shown that Fe_2O_3 powder start to crystallise as γ-Fe_2O_3, MgO powder as periclase, TiO_2 as anatase and Al_2O_3 as γ- Al_2O_3, obtained from the initial pseudo-boehmite decomposition.

In the case of MgO powder, after anneling, the presence of high amount of adsorbed CO_2 was noticed (1500, 1410, 870 and 650 cm^{-1}), underlying the great tendency of the nano-sized MgO powder to uptake CO_2 form atmosphere.

Table 2 shows the structural and textural properties versus thermal treatment of powders.

Table 2. Structural and textural properties versus thermal treatment of the powders studied in this paper.

Sample	Temperature of thermal treatment	Phase composition	Specific surface area BET (m^2/g)
TiO_2	initial	tendency of anatase crystallisation	145.11
	300 °C	weak crystallizated anatase	154.18
	800 °C	Rutile + anatase (little)	< 3
AlO(OH)	initial	tendency of pseudo-boehmite crystallization	127.5
	450 °C	weak crystallized boehmite	183.65
	800 °C	γ-Al_2O_3	111.36
MgO	initial	amorphous	93.48
	450 °C	tendency of MgO crystallization	
	800 °C	MgO (periclase)	< 3
Fe_2O_3	initial	Amorphous	174.65
	450 °C	γ-Fe_2O_3	
	800 °C	α-Fe_2O_3	< 3

Much higher surface area at the intermediate temperatures may be assigned to the structural OH^- elimination, according to the thermal analysis results. With increase of temperature the surface area decreases. The great tendency of crystallization of TiO_2, Fe_2O_3 and MgO samples is confirmed by low values of specific surface at 800 °C and is presented in Fig. 4.

TEM micrographs from Al_2O_3 and TiO_2 samples presented in Fig. 5 confirm the presence of nano-sized powders.

4. Discussion

Sol-gel processing offers the possibility to control, the synthesis of powders with more and more elaborate characteristics: size, shape, as well as hierarchical internal structure.

According to the general principles of sol-gel powders preparation, high amount of water and a neutral or basic values of pH (see Table 1) were used in order to obtain the Al_2O_3, TiO_2, MgO and Fe_2O_3 powders.

The thermal stability of the obtained oxides is different and increases in the order TiO_2<MgO<Fe_2O_3<Al_2O_3. TiO_2 gel losses the water and organic residues up to 300 °C, while other gels need, in order to eliminate these adsorbed molecular species (Fig. 1), an annealing up to 450 °C.

The thermal treatment of the oxide powders do not change the particle size, but decreases their tendency to aggregation.

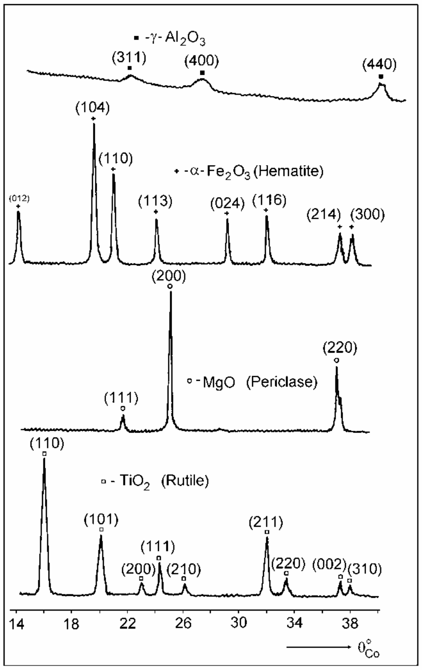

Fig. 4. XRD results on DTA/TGA residues at 1000 °C.

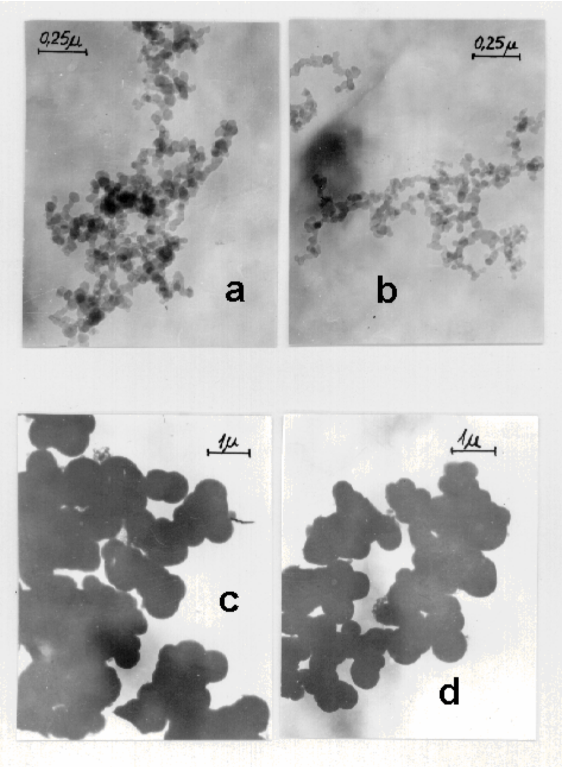

Fig. 5. TEM micrographs of Al_2O_3 (a - initial; b - annealing 1h at 450 °C) and TiO_2 samples (c - initial; d - annealing 1h at 300 °C).

The IR spectra results (Fig. 2) evidenced the formation of M-O-M bonds in solution.

The high values of specific surface area (Table 2) confirm that primary particles are characterized by internal pore network; they can be described by an aggregation of smaller solids units. Also, aggregation has no reason to stop at the primary particles level. A hierarchy of aggregates which associates bigger and bigger units must be considered from electrostatic and steric interactions. The high values of specific surface area confirm also the reactivity of powders.

The surface area and the particle size depend also on the type of oxides obtained. Between the surface area and the particle size do not exist a direct correlation due to the presence of an internal pore network and aggregation tendency, mentioned above.

Al_2O_3 sample has the lowest tendency of crystallization (see Fig. 4) according to the greatest surface area values even at 800 °C. MgO sample has a greatest tendency of crystallization according to the smaller surface area of the initial oxide.

In the used experimental conditions amorphous, nano-sized and monodisperse sol-gel powders have been obtained in Al_2O_3, TiO_2, MgO, Fe_2O_3 monocomponent system.

5. Conclusions

Sol-gel monocomponent powders have been obtained in Al_2O_3, TiO_2, MgO, Fe_2O_3 monocomponent system.

In the used experimental conditions the powders obtained were amorphous, nano-sized and monodisperse.

Such powders may be used as raw materials for advanced polycrystalline ceramics preparation, as pigments, catalysts or support in chromatography.

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