Intercluster porous nanocomposites from combination of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation and Anderson-type $[Al_{1-x}Cr_xMo_6O_{24}H_6]^{3-}$ anion: XRD, TG-DTA, SEM-EDAX and EPR studies

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Abstract The synthesis of intercluster porous nanocomposites obtained from polyoxometallate compounds such as the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation (named Al₁₃) and the Anderson-type $[Al_{1-x}Cr_xMo_6O_{24}H_6]^{3-}$ anion (named $Al_{1-x}Cr_xMo_6$) has been performed in order to study the interaction between the two cluster ions, the stability of the XMo₆ planar configuration, the products obtained after thermal treatment, the structure and the local symmetry of the Cr³⁺ species. Chemical, thermal, structural and spectroscopic characterizations of the original and thermally treated phases have been followed by different techniques such as TG-DTA, XRD, SEM-EDAX, and mainly by EPR. All the results have shown that the structure of the intercluster nanocomposites $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ precursors is similar to that reported by Son et al. for the chromium-free (Al₁₃)(AlMo₆)₂ intercluster nanocomposite [Son et al., J. Am. Chem. Soc. 122 (2000) 7432]. After thermal treatment in air at several temperatures of the $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ nanocomposites the following phases have been observed and characterised: (i) at 400 °C an amorphous phase containing dispersed Cr³⁺ ions; (ii) at 700 °C a crystalline phase corresponding to Cr2(MoO4)3/Al2(MoO4)3 solid solutions; (iii) at 950 °C α-Al₂O₃/Cr₂O₃ solid solutions with a random dispersion of the Cr^{3+} ions.

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1 Introduction

New materials obtained from the combination between inorganic cationic and anionic clusters have been recently reported. Inorganic monolithic gels containing $[V_{10}O_{28}]^{6-}$ or $[Mo_7O_{24}]^{6-}$ anions and the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation (named Al₁₃) are known as intercluster nanocomposites because the clusters identity seems to remain almost intact. They can be prepared from salts of the isopolyoxometalates with a simple approach of mixing aqueous solutions of the clusters, as reported in literature [1]. The $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}][AlMo_6O_{24}H_6]_2(OH)$. 29.5H₂O nanocomposite obtained from ammonium heptamolybdate and Al₁₃ suggests interesting possibilities in designing new solid-state materials, particularly for catalytic purposes. In fact, the Al incorporation as heteroelement in the isopolymolybdate building block leads to the formation of the $[AlMo_6O_{24}H_6]^{3-}$ Anderson-type anion (named AlMo₆), which is uniformly located into the Al-rich arrangement. The Anderson phase (NH₄)₃ [Co- $Mo_6O_{24}H_6] \cdot 7H_2O$ supported on γ -alumina has proved to be an interesting alternative route for the preparation of $Co-Mo/\gamma-Al_2O_3$ HDS catalysts [2]

The aim of this work is the synthesis of the nanocomposites from the direct interaction between the Al_{13} cation with the $Al_{1-x}Cr_xMo_6$ anion and the chemical, thermal and spectroscopic characterization of the original and thermally treated phases by different techniques (TG-DTA, XRD, SEM-EDAX and EPR). We focused the attention on the study by XRD and mainly by EPR spectroscopy to recognize the structure and the local symmetry of the Cr³⁺

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species in the diluted system and to examine: (a) the interaction with the Al-matrix, (b) the stability of the XMo_6 planar configuration, (c) the thermal products.

2 Experimental

2.1 Samples preparation and treatments

Cr-containing samples of general formula $[AlO_4Al_{12} (OH)_{24}(H_2O)_{12}][Al_{1-x}Cr_xMo_6O_{24}H_6]_2 (OH) \cdot 29.5H_2O$ with $x = 0, 0.01, 0.1, 1, named (Al_{13})(Al_{1-x}Cr_xMo_6)_2$, were prepared by mixing at RT solutions of the Al₁₃ cation and of the Anderson type $Al_{1-x}Cr_xMo_6$ anion. The Al₁₃ solution was prepared by controlled hydrolysis of AlCl₃ according to the literature method [3] and the Al_{1-x}Cr_xMo₆ solutions by the general procedure described previously [4].

All the $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ samples were then thermally treated in air at several temperatures (400, 750 and 950 °C) for 5 h.

2.2 XRD measurements

XRD measurements were performed by a Philips PW 1729 diffractometer (CuK α , Ni-filtered radiation) equipped with an IBM computer (software APD-Philips for data treatment).

2.3 Scanning electron microscopy (SEM-EDAX)

Samples were analyzed in a Philips 505 electron microscope with an EDAX 9100 microprobe analysis (energy dispersive detector).

2.4 EPR measurements

The EPR measurements were recorded at RT and in some cases, as indicated in the text, at -196 °C, on a Varian E-9 spectrometer (X-band), equipped with an on-line computer for data treatment. The absolute concentration of the paramagnetic species was determined from the integrated area of the spectra recorded at RT, using as standard the Varian strong pitch (5[·]10¹⁵ spin cm⁻¹). This secondary standard was accurately calibrated by a series of primary standards [5]. The standard and the samples, as powder, were placed in the EPR silica tube (i.d. 3 mm) in a weighed amount to fill the resonant cavity completely in order to have "full length geometry". In these conditions the numbers of spin cm⁻¹, *N*, of two samples *a* and *b* are related by the equation:

$$N_a = N_b \frac{g_b}{g_a} \frac{S_b(S_b+1)}{S_a(S_a+1)} \cdot \frac{A_a}{A_b} \tag{1}$$

where A are the integrated areas normalized for the instrumental conditions, g the g-values, and S the spin. N_a

was then divided by the linear density $(g \text{ cm}^{-1})$ of the sample in the EPR tube to yield the concentration of paramagnetic species (spin g^{-1}). This value was then converted in the units reported in Table 2. The *g* values were determined taking as reference the sharp peak at g = 2.0008 of the E'₁ center (marked with an asterisk in Figs. 2 and 5); the E'₁ center was formed by UV irradiation of one of the silica dewars used as sample holder [5].

3 Results

3.1 As prepared samples

The crystallinity of the Cr-containing samples was found by XRD to strongly decrease with increasing chromium content. Figure 1 shows the XRD pattern for the highly crystalline (Al₁₃)(Al_{0.99}Cr_{0.01}Mo₆)₂ sample. The spectrum is very similar to the powder XRD pattern of the Cr-free (Al₁₃)(AlMo₆)₂ parent compound, whose structural features were described by Son et al. [1]. The presence of so many reflections at low 2θ angles confirms what it was reported regards the low symmetry (monoclinic) and the large unit cell volume ($V \approx 10600 \text{ Å}^3$) exhibited by (Al₁₃)(AlMo₆)₂ [1].

Scanning electron microscopy (SEM-EDAX) was useful to analyze comparatively the morphology and chemical composition. SEM results (not reported) showed typical prismatic particles with sizes of ~10 and lower



Fig. 1 XRD pattern of the sample $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ with x = 0.01

Sample	% Al ^a		% Mo ^a		% Cr ^a	
	Nom.	Exper.	Nom.	Exper.	Nom.	Exper.
(Al ₁₃)(AlMo ₆) ₂	26.01	26.56	73.99	74.24	_	_
(Al ₁₃)(Al _{0.99} Cr _{0.01} Mo ₆) ₂	25.97	27.54	73.97	72.46	0.067	b
$(Al_{13})(Al_{0.9}Cr_{0.1}Mo_6)_2$	25.58	24.32	73.75	74.60	0.67	1.07
(Al ₁₃)(CrMo ₆) ₂	23.13	24.39	70.50	69.16	6.37	6.42

Table 1 SEM-EDAX data for the $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ nanocomposites

^a % element is the relative weight percent of the three elements. ($\%_{Al} + \%_{Mo} + \%_{Cr} = 100$)

^b Value not detected by the equipment

than 3 μ for Al and Cr composites, respectively. This is in agreement with the trend to colloidal nature of composite materials [6]. The EDAX data show a good agreement between nominal and experimental elemental contents (Table 1).

The EPR spectra, recorded at RT, of two samples, (x = 1 and 0.1) are reported in Fig. 2. The spectrum of the x = 1 sample is relatively simple showing a 3-g value signal $(g_1 = 4.21, g_2 = 3.96, g_3 = 1.93)$ with a weak shoulder at $g_4 = 5.96$ (Fig. 2a). This spectrum is quite intense but the lines are rather broad. A considerable sharpening of the linewidth occurs when the paramagnetic Cr species is diluted with a diamagnetic Al ion, sample x = 0.1; moreover, each component of the 3-g value signal splits in several lines (at least two or possibly three), Fig. 2b. The spectra recorded at -196 °C remained substantially unchanged.



Fig. 2 EPR spectra of the as prepared samples $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$: (a) x = 1.0; (b) x = 0.1

The pattern of the EPR spectrum of powder samples containing Cr^{3+} species (3d³ ion; S = 3/2) essentially arises from the effect of the fine structure terms, *D* and *E*. In fact the anisotropy of the *g* factor is quite small and can be neglected: we assume an isotropic value of $g_0 = 1.98$.

The spectrum is quite complex when the *D* term is near to the microwave photon energy, hv, ($hv \approx 0.33$ cm⁻¹ at X band), namely when $hv/D \approx 1$; a considerable simplification occurs when this ratio is high (small D term) or low (high D term). In this last case a 3-g value signal is observed, whose components correspond to the resonance along the X, Y and Z axes between the lower 1-2 Kramer doublet. The effective g values (g_{eff}) are almost independent from hv/D, depending only on the E/D ratio. In the case of axial symmetry (E/D = 0), $g_{xx} = g_{yy} = g_{\perp}$, $g_{zz} = g_{\parallel}$ and at first order $g = 2 g_{0}$ and $g_{\parallel} = g_{0}$ [7]. The signal of the x = 1 sample shows a small deviation from the axial symmetry. The presence of two distinct g_{xx} and g_{yy} values is demonstrated by the small inflection of the g_{\perp} component. The weak and sharp peak at $g_4 = 5.96$ (Figs. 2a and 2b) arises from the resonance of the upper 3-4doublet along the Z-axis (Z₃₄ transition), which at first order occurs at $g = 3 g_0$. Because in axial symmetry Z_{34} has zero transition probability, it is absent in axial symmetry and appears when a deviation from it occurs.

From the g_{eff} values and with the help of the diagrams reported by Van Reijen [8] or by direct calculation, it is possible to evaluate the *E/D* and *hv/D* ratios. From this analysis we obtained: E/D = 0.06 and $D = 1 \text{ cm}^{-1}$.

In the Cr dilute sample (x = 0.1), the sharpening and the splitting of the 3-g signal indicates the existence of several sites with small difference of the *E/D* ratio. By contrast the g_4 peak remains a single and sharper peak. This is due to the fact that the Z_{34} transition has a very small dependence on *E/D* [8].

3.2 Samples thermally treated in air

Thermal treatments in air at increasing temperatures cause the decomposition of the nanocomposites by release of



Fig. 3 TG-DTA pattern of sample $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ with x = 1

volatile products. This is clearly shown by the TG-DTA curves related to sample with x = 1, $(Al_{13})(CrMo_6)_2$ (Fig. 3).

A first weight loss, accompanied by a strong endothermic peak, occurs up to 400 °C, corresponding to the elimination of water. The solid residue obtained at 400 °C, as shown by the XRD pattern reported in Fig. 4, is amorphous. In the range 400–800 °C where no weight loss is observed, the crystallization occurs, as evidenced by the exothermic peak at 600 °C in sample x = 1, $(Al_{13})(Cr-Mo_6)_2$, and by the corresponding XRD pattern (Fig. 4). The formation of the crystalline phase starts at 600 °C and reaches its maximum value at 800 °C. From the literature data [9] the XRD pattern of the crystalline phase corresponds to those of $Cr_2(MoO_4)_3$ and $Al_2(MoO_4)_3$, which are isomorphous, or more probably to their solid solutions. A second weight loss, accompanied by another strong endothermic peak, occurs at higher temperature and corresponds to the decomposition of the molybdate phase with release of volatile MoO_3, in agreement with that found in $(Al_{13})(AlMo_6)_2$ [1]. The residue non-volatile solid at 950 °C is well crystallized as α -Al₂O₃ and α -Cr₂O₃ or their solid solutions (Fig. 4).

The EPR spectra of thermally treated $(Al_{13})(Al_xCr_{1-x} Mo_6)_2$ samples with x = 0.1 and 1 are shown in Figs. 5 and 6, respectively. The spectrum of $Cr_2(MoO_4)_3$ is included for comparison in Fig. 6.

The thermal treatments deeply alter the EPR spectra of both samples.

In the more diluted sample (x = 0.1), after treatment at 400 °C, the spectrum is poorly resolved and consists of a broad and asymmetric resonance from $g \approx 5$ to $g \approx 2$ and of a sharp peak at g = 1.96 (Fig. 5a). The broad resonance is typical of isolated Cr³⁺ ions in an amorphous matrix or on the surface [10], and the sharp peak is typical of Cr⁵⁺ ions [10]. Since the integrated area of the sharp peak is small respect to the total area, Cr⁵⁺ represents a minor



Fig. 4 XRD patterns of sample $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ with x = 1, as prepared and after thermal treatment at 400, 700, and 950 °C



Fig. 5 EPR spectra of sample $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ with x = 0.1, after thermal treatment at: (a) 400 °C, (b) 700 °C, (c) 950 °C

component, even if in the first derivative presentation it dominates. After treatment at 700 °C the spectrum becomes complex, showing the most intense peaks at $g_{\text{eff}} = 12, 5.32, 4.78, 2.81, 1.97, 0.92, \text{ and } 0.81$ (Fig. 5b). When $hv/D \approx 1$ (see above), the spectrum becomes complex and the transitions between the 2-3 spin levels fall at very high g_{eff} values (>10), namely at very low fields, as the presence of the first peak at $g_{\text{eff}} = 12$ (H = 540 G) indicates. The analysis of the spectrum in this case is more difficult and somewhat uncertain: we estimate E/D = 0.25 and hv/D = 1.4. Anyway this is a spectrum typical of Cr³⁺ ions in sites of well-defined symmetry, thus it must be assigned to isolated Cr³⁺ ions in a crystalline phase. The EPR spectrum of isolated Cr³⁺ ions suggests that the crystalline phase detected by XRD after treatment at 700 °C (Fig. 4) is indeed a Cr₂(MoO₄)₃/Al₂(MoO₄)₃ solid solution. After treatment at 950 °C, the EPR spectrum, Fig. 5c, corresponds to that of isolated Cr^{3+} ions into α -Al₂O₃, often reported in literature [5, 8]. The spectrum has been analyzed with the fine-structure terms D = -0.1930 cm⁻¹ and E/D = 0, determined on ruby single crystal [11]. Besides the peaks assigned to the isolated Cr^{3+} ions, a symmetrical peak at g = 1.98 ($\Delta H_{pp} = 460$ G) is present, assigned to clustered Cr^{3+} ions in α -Al₂O₃ [5].

In the more concentrated Cr sample (x = 1), after treatment at 400 °C (Fig. 6a) the 3-g value signal disappeared and the spectrum consists of a broad band ($\Delta H_{\rm pp} \approx 1000$ G centered at g = 1.98) with a shoulder at



Fig. 6 EPR spectra of sample $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ with x = 1, after thermal treatment at: (a) 400 °C, (b) 700 °C, (c) 950 °C. The EPR spectrum of $Cr_2(MoO_4)_3$ is reported in (d) for comparison

 $g \approx 5$ and a sharper peak ($\Delta H_{pp} \approx 250$ G at g = 1.96). We assign the broad resonance and the shoulder at $g \approx 5$ to clustered and isolated Cr³⁺ ions, respectively, and the sharper peak to Cr⁵⁺ dispersed in the amorphous matrix or on the surface. After treatment at 700 °C (Fig. 6b) the spectrum consists of a single and symmetrical line of Lorentzian shape at g = 1.98. Pure Cr₂(MoO₄)₃ shows a similar spectrum (Fig. 6d). Since many Cr-containing systems give a single exchange narrowed line, for a more confident assignment of this signal, we recorded both the spectra at two temperatures (RT and -196 °C). Both the spectra undergo to a similar broadening: the linewidth (ΔH_{pp}) increases from 480 at RT to 700 G at -196 °C in the sample with x = 1 and from 420 G at RT to 650 G at – 196 °C in pure Cr₂(MoO₄)₃. After treatment at 950 °C (Fig. 6c) the spectrum shows an even more intense signal constituted of a single and symmetrical line of Lorentzian shape at g = 1.98 ($\Delta H_{pp} = 530$ G). Taking into account the XRD characterization, we assign this signal to exchange coupled Cr^{3+} ions in solid solution in α -Al₂O₃. Due to the higher Cr content no signals of isolated Cr³⁺ ions were detected.

Quantitative EPR measurements yield additional information (Table 2). Whereas in pure $Cr_2(MoO_4)_3$ the Cr^{3+} concentration is not far from the theoretical value (92%), in the $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ as prepared samples it corresponds to $\approx 50\%$ of the nominal content. The cause of this discrepancy arises from the high D term, which renders inaccessible the transitions between the higher Kramer doublets. As far as the thermally treated samples, the percentage of Cr³⁺ is near to the nominal value in those treated at 700 °C, whereas in the others it is significantly lower. In the amorphous samples obtained after treatment at 400 °C a large fraction of the isolated ions escapes to the EPR detection, because of the variability of the site symmetry. This cause is more important for the diluted sample (x = 0.1), which has an higher fraction of isolated ions. In the samples treated at 950 °C, because of the high Neel temperature of α -Cr₂O₃ and of its concentrated solid solutions, the Eq. 1, which is based on the simple Curie Law, gives an underestimate, which increases by increasing the Cr content [5].

4 Discussion

All the experimental techniques used in this work confirm that the structure of the intercluster nanocomposites $(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ is that reported by Son et al. for the chromium-free $(Al_{13})(AlMo_6)_2$ compound [1]. It may be recalled that the structure of $(Al_{13})(AlMo_6)_2$, determined by single crystal XRD by Son et al. [1], consists of two building block clusters, Al_{13} and $AlMo_6$. Two types of

Table 2 Absolute Cr ³⁺ concentration in	Sample	$[Cr^{3+}]^{a}_{nom.}$ wt%	$[Cr^{3+}]_{EPR}$ wt%	% Cr ^{3+ b}
$(Al_{13})(Al_{1-x}Cr_xMo_6)_2$ nanocomposites evaluated by quantitative EPR measurements	$(Al_{13})(Al_{0.9}Cr_{0.1}Mo_6)_2$ as prepared	0.29	0.14	49
	$(Al_{13})(Cr Mo_6)_2$ as prepared	2.87	1.35	47
	(Al ₁₃)(Al _{0.9} Cr _{0.1} Mo ₆) ₂ treated at 400 °C	0.42	0.09	22
	(Al ₁₃)(Cr Mo ₆) ₂ treated at 400 °C	4.09	2.3	56
^a Calculated taking into account the elimination of volatile fraction at 400 °C (H ₂ O) and at 950 °C (MoO ₃) ^b % Cr ³⁺ = $100 \times [Cr^{3+}]_{EPR}/$ [Cr ³⁺] _{nom}	(Al ₁₃)(Al _{0.9} Cr _{0.1} Mo ₆) ₂ treated at 700 °C	0.42	0.35	83
	(Al ₁₃)(Cr Mo ₆) ₂ treated at 700 °C	4.09	3.6	88
	(Al ₁₃)(Al _{0.9} Cr _{0.1} Mo ₆) ₂ treated at 950 °C	1.35	1.1	81
	(Al ₁₃)(Cr Mo ₆) ₂ treated at 950 °C	12.8	7.1	55
	Cr ₂ (MoO ₄) ₃	17.8	16.4	92

crystallographically different but chemically identical AlMo₆ clusters are present, called AlMo₆-I and AlMo₆-II. The structure is characterized by layers formed by Al₁₃ and AlMo₆-I clusters parallel to the *bc*-plane of the monoclinic cell and AlMo₆-II pillars between the above layers. An empty space between the pillars leads to intersecting two-dimensional channels running parallel to the bc-plane. The channel dimensions, $3.1 \times 5.9 \text{ Å}^2$ and $6.2 \times 3.9 \text{ Å}^2$ for the smallest and widest cross-sectional areas, respectively, are comparable to those of zeolites. The two building block clusters, the Al₁₃ cation and the AlMo₆ anion, form therefore an ionic crystal packed to maximize the contacts between the oppositely charged ions. The arrangement of these bulky ions leads to an open structure with channels containing water molecules and OH⁻ ions. The water molecules can be eliminated by vacuum drying at RT. The elimination of water renders the sample amorphous but the original structure is recovered on rehydration [1].

Due to the very fast reaction between ions, the mixing of aqueous solutions of Al_{13} and $AlMo_6$ ions leads in general to the formation of an amorphous precipitate. Indeed to obtain a crystalline product, Son et al. [1] added to Al_{13} an ammonium heptamolybdate solution (containing the Mo_7 anion), which in presence of Al_{13} slowly converts into the AlMo₆. The Anderson polyanion $[XMo_6O_{24}H_6]^{3-}$ (X = heteroatom, Al or Cr in our case) is constituted by a hexagonal planar arrangement of seven octahedra MO₆, the central one containing the heteroatom (M = X) and the others six octahedra containing molybdenum ions. To prepare our nanocomposites it is not possible to use the procedure described by Son et al., because of the requirement of the insertion in a controlled way of Cr^{3+} into the Anderson anion.

A strong evidence supporting the structure of our samples came from the EPR results: indeed the EPR spectra of the as prepared samples are quite similar to those of the Cr-Anderson phase [12] and the fine structure terms, in particular the E/D ratio, are about the same. Thus, even if the

samples with x = 1, $(Al_{13})(CrMo_6)_2$, and x = 0.1, $(Al_{13})(Al_{0.9}Cr_{0.1}Mo_6)_2$, are amorphous, their EPR spectra are similar to those of polycrystalline samples. This means that the Cr^{3+} ion is located in sites of well defined symmetry, namely the configuration of the Anderson anion is preserved in the nanocomposites. Moreover the sample with x = 0.01, $(Al_{13})(Al_{0.99}Cr_{0.01}Mo_6)_2$, which results by XRD to be highly crystalline (see Fig. 1), gives practically the same EPR spectrum as the sample with x = 0.1: its low intensity, due to the low Cr content (0.029 wt%), does not afford to record spectra of good quality.

The presence in these nanocomposites of a paramagnetic species located in the Anderson-type heteropolyanion, substantially isolated from the other magnetic ions, hinders the establishment of exchange interactions between them also in the most concentrated sample (x = 1), as occurs, on the contrary, in oxide systems [for instance solid solutions α -Al₂O₃/Cr₂O₃ and Al₂(MoO₄)₃/Cr₂(MoO₄)₃]. In these exchange-coupled systems the fine structure disappears and the EPR spectrum changes to a single exchange narrowed line with Lorentzian shape. In the undiluted compound is operative only the long range dipolar interaction which preserves the fine structure and causes line broadening being of the order of $g\beta/r^3$, namely of about 100 G (r is the average distance between the paramagnetic species). The dilution with a diamagnetic ion such as Al^{3+} (sample with x = 0.1) causes an increase of r and then a sharpening of the spectrum.

The XRD and EPR techniques give also a detailed picture of the evolution of the system when submitted to thermal treatments in air.

After treatment at 400 °C the nanocomposites, in agreement with previous study on $(Al_{13})(AlMo_6)_2$ [1], released all the water (with a weight loss of 30%) and the solid residue is amorphous. The EPR spectra, although poorly resolved, indicate the presence of isolated and clustered Cr^{3+} ions and of Cr^{5+} as a minor component, but a large fraction of the isolated Cr^{3+} ions escapes to the EPR detection.

At 700°C a well-crystallized phase was detected by XRD and the EPR spectrum of diluted sample (x = 0.1) indicates that the Cr³⁺ ions are all isolated, thus well dispersed in the Al₂(MoO₄)₃/Cr₂(MoO₄)₃ solid solution. It must be observed that the experimental value E/D = 0.25, near to 1/3 (rhombic symmetry), is in agreement with the crystal structure of Cr₂(MoO₄)₃ (orthorhombic).

Since in the nanocomposites the (Al + Cr)/Mo atomic ratio is higher than that present in the molybdate phase (the ratio being 5/4 and 2/3, respectively), after treatment at 700 °C the excess of trivalent ions must be present as an X_2O_3 phase. However, no evidence of this phase was found by XRD: therefore it must be an amorphous or highly dispersed phase. The complete miscibility of Al and Cr both in Al₂O₃/Cr₂O₃ and Al₂(MoO₄)₃/Cr₂(MoO₄)₃ solid solutions suggests that the Cr³⁺ ions are distributed in both phases. However, the EPR analysis detected no signals attributable to Cr³⁺ ions in the Al₂O₃/Cr₂O₃ phase. In particular, in the diluted sample (x = 0.1) where the Cr³⁺ ions are essentially isolated, the presence of a highly dispersed, but crystalline phase, should be detectable. Therefore it can be concluded that excess of trivalent ions are in the form of an amorphous Al_2O_3/Cr_2O_3 phase.

Finally at 950 °C the XRD detected a well crystallized α -Al₂O₃ phase and the EPR indicated that in diluted sample (x = 0.1) the Cr³⁺ ions are mainly isolated, with a small fraction of clustered (exchange-coupled) ions, whereas in the concentrated one (x = 1) the Cr³⁺ ions are all clustered. Considering that the nominal Cr content of the solid residue is for the two samples 1.35 and 12.8 wt%, respectively, these results are in good agreement with those obtained on α -Al₂O₃/Cr₂O₃ solid solutions prepared by impregnation of γ -Al₂O₃ with Cr(NO₃)₃ solutions and by firing at increasing

temperatures up to 1200 °C [5]. By assuming a random distribution of the magnetic ions, it was calculated that in these solid solutions a Cr^{3+} ion can be considered isolated if no other Cr^{3+} ions are at a distance shorter than r = 0.63 nm, a value similar to those found for several paramagnetic ions (Cr^{3+} , Fe^{3+} , Mn^{2+} , Co^{2+}) in different matrices (α -Al₂O₃, β -Ga₂O₃, NaAlO₂, bismuth molybdovanadates, ZnS, MgO) [5]. As far as our system is concerned, the conclusion is that after the treatment at 950 °C in air α -Al₂O₃/Cr₂O₃ solid solutions with a random dispersion of the Cr³⁺ ions are formed.

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