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EXAFS and XANES characterization of silicate-oxide nanocomposites

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X ray absorption edges and preedges together with Fourier transforms of the EXAFS signal of the $LaCo(fsa)_2en,NO_3$ complex ($(fsa)_2en$ = N,N'-bis(3-carboxysalicydene)ethylenediamine) alone or intercalated in montmorillonite and taeniolite have been studied as a function of temperature. A preferential orientation of the complex has been found when it is intercalated in the silicates. Upon applying thermal treatment, it undergoes similar decomposition whatever it is free or in taeniolite. Due to the thermal stability of taeniolite layers, a taeniolite-$LaCoO_3$ layered nanocomposite could be formed. On the other hand, we have shown that being in montmorillonite, the cobalt oxide phase is reduced progressively above 270°C.

Keywords : taeniolite, montmorillonite, oxide, perovskite, lamellar nanocomposite, EXAFS, XANES.

INTRODUCTION

Previous attempts have shown a noticeable increase of the surface area and catalytic activity of "perovskite pillared" montmorillonite in comparison with pure perovskite[1]. Therefore, we were interested in elaborating nanocomposites made of La_xMO_y oxides dispersed in a layered silicate matrix.

The preparation of the silicate-oxide nanocomposites requires a low temperature thermal treatment allowing the formation of an interlayer oxide without

damaging the host structure. The most recent method used to prepare them is the thermal decomposition of an intercalation compound consisted of an organometallic heterobinuclear complex between the layers of a lamellar silicate (montmorillonite or taeniolite)[2-5].

In this paper, we report data on EXAFS and XANES characterizations of silicate/oxide nanocomposites showing the different behaviors of $LaM^{\circ}(fsa)_2en,NO_3$ complex heated alone or in a constrained medium (montmorillonite or taeniolite). We present FT only. Refinements are carried out and will be published later.

EXPERIMENTAL

For the characterization, we prepared powders of the organometallic complex according to the experimental mode described in reference[4]. For the exchange with the alkali interlamellar cations of silicates, the appropriate amount of $LaCo(fsa)_2en,NO_3.H_2O$ complex (1.2 CEC) was soaked in a 1% aqueous suspension of clay (Li-Taeniolite : Topy Industry, Japan, CEC=262meq/100g, Na-Montmorillonite : Wyoming, CEC=87meq/100g), and the mixture was stirred for several days at 60°C. After repeated washing with water and separation by centrifugation, films of the $LaCo(fsa)_2en$-Clay compounds were prepared by sedimentation. The X ray absorption experiments were carried out with the synchrotron radiation of the D.C.I. ring (E_{orb}=1.85KeV) at LURE (Orsay, France). EXAFS and XANES spectra were recorded respectively in the range 7500-8700eV (step 2eV) and 7700-7750eV (step 0.2eV) at the K edge of Cobalt (standardization with a cobalt sheet : beginning of the jump at 7709eV ; maximum at 7734eV) with a 311 silicon monochromator. All the experiments were carried out at 10K, in order to improve the resolution of the spectrum by minimizing the Debye-Waller factor. The absorption edge position was taken at half height of the jump. EXAFS spectra were normalized with a theoretical function : $J(1-8*(E-E_{edge})/3*E_{edge})$. Kaiser type weighting windows were used (τ=3) for the calculation of the Fourier transform of $k^3\chi(k)$

RESULTS and DISCUSSION

$LaCo(fsa)_2en,NO_3$ complex

It has been previously shown that the $LaCo(fsa)_2en,NO_3$ complex is a good precursor for the low temperature synthesis of a perovskite type oxide[3]. Under oxygen atmosphere, the $LaCoO_3$ oxide appears as a major phase at about 400°C. Edges, preedges and Fourier transforms of the EXAFS signal of $LaCo(fsa)_2en,NO_3$ treated at different temperatures were compared to those of Co_3O_4 and $LaCoO_3$ perovskite reference prepared by the rare earth method[7].

The absorption spectrum of the non-heated complex presents 3 maxima in the 7725-7740eV region, which are characteristic of a low spin state[8]. We can consequently conclude that it exhibits a partial "high spin-low spin" transition which could be temperature induced upon cooling the sample to 10K as reported for $CoH_2(fsa)_2en,(H_2O)_2$ [8-10]. For samples prepared above 250°C, the shape of the spectra is more characteristic of high spin states.

At 300°C, the preedge region is very similar to that of Co_3O_4 (fig.1). The presence of a plateau is explained by the sum of the contributions of mixed valences, which in the case of Co_3O_4 are attributed to tetraedral and octaedral sites, $(Co^{2+})_T(Co^{3+}{}_2)_{Oc}O_4$. Preedge region of the complex heated above 600C°C is comparable to the perovskite reference ($LaCoO_3$).

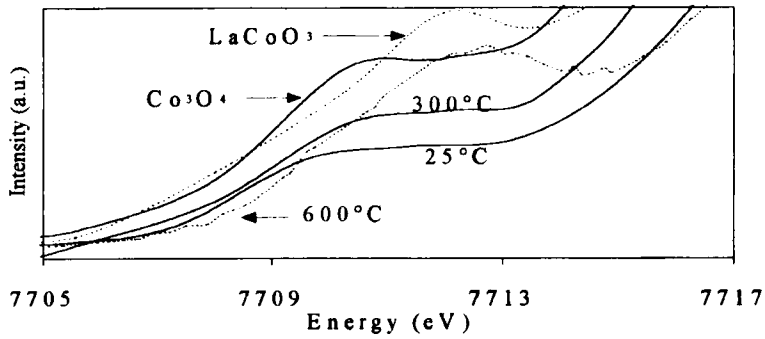

Figure 1 Preedge region in the X ray absorption spectrum of the complex heat-treated at various temperatures.

Because of the spin transition, the edge of the complex is shifted to high energies below 25°C[11] (Table I). The 3.5 eV increase between 250°C and 1000°C corresponds to the Co^{2+} to Co^{3+} transformation[11]. When the thermal treatment was performed under air, the edge value increased of about 2eV between 250 and 400°C, due to only partial oxidation of cobalt from Co^{II} to Co^{III}. On the other hand, under oxygen atmosphere, oxidation is completely achieved at 400°C, leading to an higher value of the edge (7721.3eV). At 600°C, the edge values are similar, whatever the kind of atmosphere used during thermal treatment. There is a good agreement between the complex heated at 1000°C and the perovskite type reference prepared by solid phase reaction (Table I).

Table I Influence of the heat treatment temperature on the Co K edge (eV) for the complex alone and intercalated in montmorillonite or in taeniolite. The edge were 7722.4eV for $LaCoO_3$ and 7719.6eV for Co_3O_4.

Temp.(°C)	25	250		300	400	500	600	700	1000
complex	7722.6	7719.1		7720.5	7720.7	7720.8	7722.7	7722.7	7722.4
Temp.(°C)	25	250	270	350	415		600	800	1000
in Mont	7722.7	7718.9	7720.0	7720.0	7718.5		7718.5	7717.8	7718.0
Temp.(°C)	25			300		500	600	700	
in Taen	7722.6			7719.9		7720.3	7720.6	7718.6	

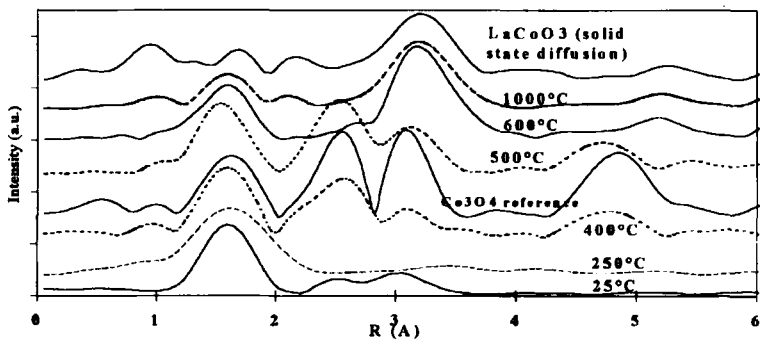

Figure 2 Fourier transforms of the EXAFS signal of $LaCo(fsa)_2en.NO_3$ after treatment at 25°C, 250°C, 400°C, 500°C, 600°C and 1000°C; Fourier transforms of references : Co_3O_4 and $LaCoO_3$.

The absence of a peak corresponding to a second neighbor on the Fourier transform of the complex at 250°C indicates that its structure is already damaged at this temperature (fig. 2). Heated at 400°C and 500°C, the product is not a pure perovskite as expected from XRD observations[3, 4], but is more compatible with a mixed valence as for example in Co_3O_4. Above 600°C, the Fourier transform of the product is quite similar to that of the perovskite reference, indicating that, from this complex, $LaCoO_3$ can be obtained at much more lower temperature than in the conventional methods.

LaCo(fsa)$_2$en-Montmorillonite

The films obtained from the samples were characterized, as a function of their orientation θ with respect to the beam (θ was defined as the angle between the beam and the normal to the plane of sedimentation (00l planes)). For the non-heated sample, as θ varies from 0° to 55°, the variations in peaks intensities and positions (fig. 3) are a good proof of the preferential orientation of the complex between the clay layers, as it was already demonstrated from X ray diffraction observations[3, 4].

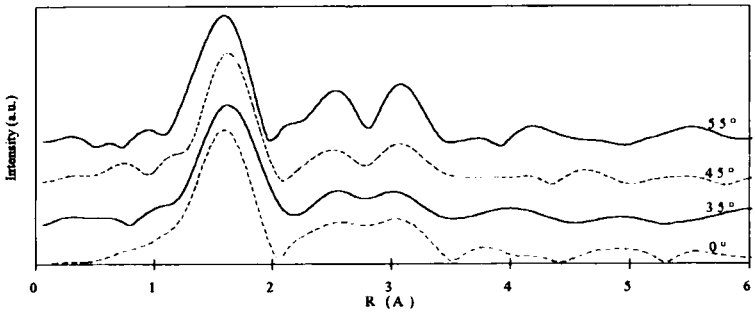

Figure 3 Fourier transform of the EXAFS signal of Mont-LaCo(fsa)$_2$en as a function of the angle θ between the beam and the normal to 00l planes.

For the samples obtained at room temperature and 250°C and for θ = 0°, the edge position and the shape of the spectrum are similar to those of the complex alone. Thus, cobalt exists as Co^{2+}, whatever the state of its derivative, free or intercalated. At 270°C and 350°C, the shift of the edge value (Table I) and the shape of the preedge region can be compared to

those of Co_3O_4 and are therefore characteristic of a mixed valence. When the temperature reaches 415°C, the preedge curve exhibits a single valence and the edge value irreversibly decreases to a value corresponding to Co^{2+}.

Thermogravimetry analysis showed a low thermal stability of the nanocomposites due to the partial dehydroxylation of the montmorillonite layers. Therefore, a reaction between hydroxyl groups and cobalt could explain the presence of reduced Co^{II}.

LaCo(fsa)$_2$en-Taeniolite

Since a montmorillonite-$LaCoO_3$ nanocomposite could not be formed, we tried to perform the synthesis of LaCo(fsa)$_2$en-Taen. Indeed, taeniolite is a synthetic silicate, with the same structure as montmorillonite but the hydroxyl groups are replaced by fluorine atoms giving a better thermal stability. Moreover, taeniolite has a Cationic Exchange Capacity about three times larger than that of montmorillonite, which can allow to prepare nanocomposites with higher oxide content.

The edge positions of LaCo(fsa)$_2$en-Taen compounds are given in table I. As for montmorillonite, the value at 20°C is the same as for the complex alone. The shape of the spectrum near the edge is typical of a low spin state. Then, upon heating, the edge position increases from 7719.9eV at 300°C to 7720.6eV at 600°C, indicating that the behavior of LaCo(fsa)$_2$en-Taen is different than that of LaCo(fsa)$_2$en-Mont. However, at 700°C the position of the edge is almost the same as for the montmorillonite derivative at the same temperature. Because of the similarity of the edge values obtained for products of thermal decomposition of the complex alone and intercalated in taeniolite below 700°C, the interlamellar phase present in taeniolite is assumed to be of perovskite type $LaCoO_3$. Above 700°C, cobalt is reduced to Co^{II} in agreement with the formation of a spinel type oxide which is the usual decomposition product of perovskites. This reduction could be due to the reaction between the "perovskite" interlamellar phase with the layers of the host matrix, as demonstrated by the thermogravimetric analysis in the range 700-800°C.

CONCLUSION

A $LaCo^{III}O_3$ perovskite oxide was formed by the pyrolysis of the $LaCo(fsa)_2en,NO_3$ complex. When the cationic part of the complex was exchanged with the Na cations of montmorillonite, a thermal treatment led to the formation of Co^{II} above 300°C, incompatible with the existence of interlamellar perovskite. This is attributed to the reduction of the interlamellar phase by the hydroxyl groups of montmorillonite. The thermal stability of the complex was improved by preparing $LaCo(fsa)_2en$-Taen nanocomposites in which the reduction of Co^{3+} to Co^{2+} occurred at higher temperatures. A taeniolite-$LaCoO_3$ nanocomposite was brought out in the 300-600°C range.

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