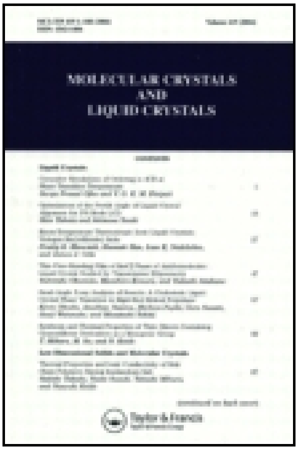

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# A Comparative Study of Silicate-Oxide Nanocomposites

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# A Comparative Study of Silicate-Oxide Nanocomposites

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$LaCo(fsa)_2en$-Montmorillonite and $LaCo(fsa)_2en$-Taeniolite ($(fsa)_2en$ = N,N'-bis(3-carboxysalicydene)ethylenediamine) derivatives have been synthesized by cationic exchange and characterized. The thermal treatment of the exchanged clays under oxidizing atmosphere led to the formation of nanocomposites above about 300°C. It has been shown that the $LaCoO_y$-Montmorillonite nanocomposite is stable up to about 550°C versus 700°C for the $LaCoO_y$-Taeniolite nanocomposite. Both are constituted of oxide pillars (diameter 20-40Å) intercalated within the silicate matrix.

Keywords : montmorillonite, taeniolite, perovskite, nanocomposite, cationic exchange.

## INTRODUCTION

During the last decades, perovskite type oxides ($LaMO_3$) were extensively applied in catalytical processes[1]. Initially, they were synthesized by grinding a stoichiometric mixture of a rare earth oxide and a metal (M) oxide, and subsequent heating at 800°C[2], or by the thermal decomposition of oxalates or cyanides[3]. The most recent method based on "chimie douce" is the thermal decomposition of heterobinuclear metallic complexes with a Schiff base as a ligand[4], but the homogeneity and the characteristics of these solids have not been controlled carefully. In a previous paper, we described improvements which allow to better control the stoichiometry of the resulting compound whatever the nature of M[5].

On the other hand, surface area and catalytic activity of perovskite "pillared" montmorillonite appear to be larger than with pure perovskite[6]. Therefore, we were interested in elaborating nanocomposites made of $La_xMO_y$ oxides dispersed in a layered silicate matrix. We developed a process based on the cationic exchange of the interlamellar cations of Na-Montmorillonite and Li-Taeniolite with $LaCo(fsa)_2en$ complex cations ($H_4(fsa)_2en$ = N,N'-bis(3-carboxysalicydene)ethylenediamine (fig. 1a) and further heat treatment leading to a nanocomposite[7,8].

In this paper, we report and compare new data on the preparation and characterization of silicate/oxide nanocomposites after the intercalation of the La-Co heterobinuclear complex into taeniolite and montmorillonite.

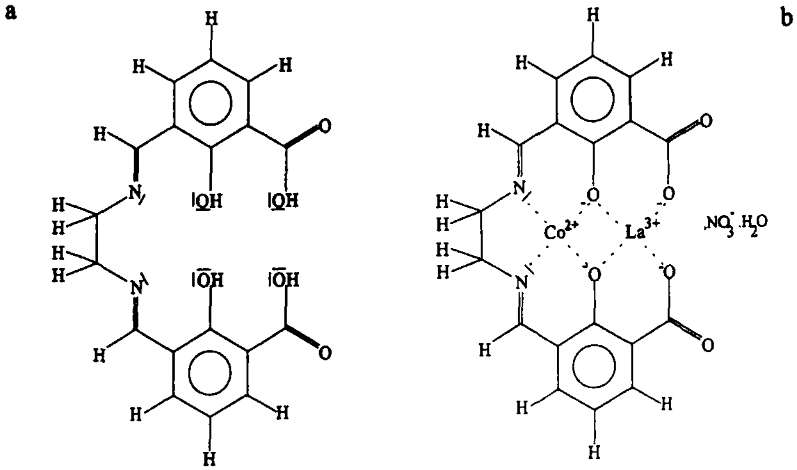

Figure 1 Schematic representation of $H_4(fsa)_2en$ (a) and $LaCo(fsa)_2en,NO_3.H_2O$ (b).

## EXPERIMENTAL

The La-Co heterobinuclear complex, noted $LaCo(fsa)_2en,NO_3.H_2O$, (fig. 1b) was synthesized according to the experimental mode described in reference[6]. 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 100 ml of 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, the LaCo(fsa)$_2$en-Clay compound was freeze dried.

Thermal treatments of LaCo(fsa)$_2$en-Clay compounds were carried out in a home made ThermoGravimetric Analysis (T.G.A.) apparatus coupled with a Balzers QMG 420 C mass spectrometer, under $O_2$/Ar (1/1, 15 ml/min) atmosphere with a 50°C/h temperature ramp. KBr pellets (0.5% dispersion in 0.1g KBr) were analyzed by infrared spectroscopy (Nicolet 710 FT-IR spectrometer) in the transmission mode. X ray diffractograms of the solid powders spread on a glass plate were recorded on a Siemens D500 diffractometer (Cu K$\alpha_1$ radiation, $\lambda$ = 1.54056 Å) in the reflection mode. Samples for TEM (Philips CM20) were ground into ethanol and dispersed into water by ultrasound for 5 minutes. A drop of the suspènsion was deposited on the thin amorphous carbon film covering the copper grid and the solvent was evaporated in a dessicator.

## RESULTS AND DISCUSSION

Atomic absorption titration of the alkali cations present in the filtrate after the reaction confirmed at least 95% exchange in all cases. A control by X ray diffraction showed that the exchange reaction is complete after 3 days. The identity period $I_c$ (22.7Å) is compatible with complex cations standing almost perpendicular to the silicate layers of LaCo(fsa)$_2$en-Mont. For the taeniolite intercalation compounds, two identity periods (24.4 and 32.0Å) were found, corresponding to two intercalated structures. Due to the high CEC of taeniolite in comparison with montmorillonite, it is suspected that complete exchange can be only achieved in taeniolite if at least a part of complex is forming a double intercalated layer.

Infrared spectra of the exchanged clays consist in the superimposition of the infrared spectra of Na-Montmorillonite (or Li-Taeniolite) and LaCo(fsa)$_2$en,$NO_3$.$H_2O$ without the narrow peak corresponding to $NO_3^-$. The absence of the peak of the $NO_3^-$ counter anion confirms that the complex has been exchanged and not only adsorbed at the surface of the clay.

The main weight loss in the thermogram of LaCo(fsa)$_2$en-Mont starts to occur at about 240°C (fig. 2) against 260°C for the complex heated alone. This small shift demonstrates a lower thermal stability of the intercalated complex due to the change of the counter anion from $NO_3^-$ to a negatively charged clay layer. Mass spectrometry of the evolved gases (fig. 2), only shows the decomposition of the organic skeleton of the complex through the release of water (m/e=18) and carbon dioxide (m/e=44). The difference between the total weight loss (23.3% after deduction of absorbed or intercalated water) and the theoretical value (19%) deduced from CEC of montmorillonite could be explained by the evolution of the OH groups of montmorillonite layers, not clearly detected at c.a. 500-600°C.

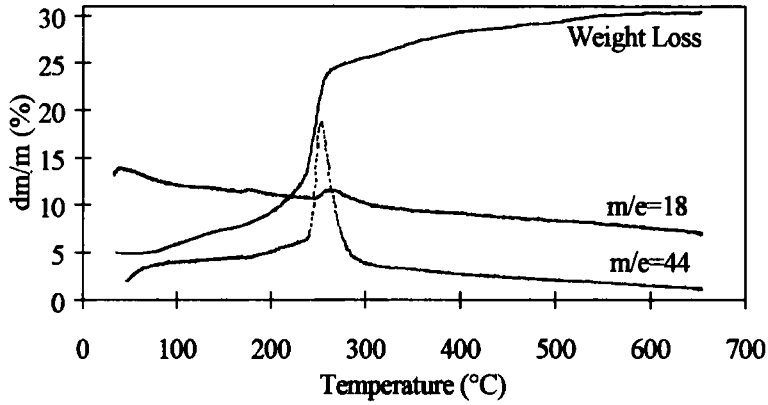

Figure 2 Thermogravimetric analysis on LaCo(fsa)$_2$en-Mont and mass spectrometry of the evolved gases.

The thermal behavior of LaCo(fsa)$_2$en-Taen (fig. 3) is similar to that of LaCo(fsa)$_2$en-Mont, however without any small slope above 500°C. As compared to montmorillonite, one must remind that the layers of taeniolite are free of OH groups. This is the reason for the absence of water evolution at high temperature. The $CO_2$ peak (m/e = 44) in the mass spectrum above 700°C is related to the decomposition of residual lanthanum oxicarbonate (as observed by X ray diffraction) which is formed during the thermal decomposition of the La-Co complex .

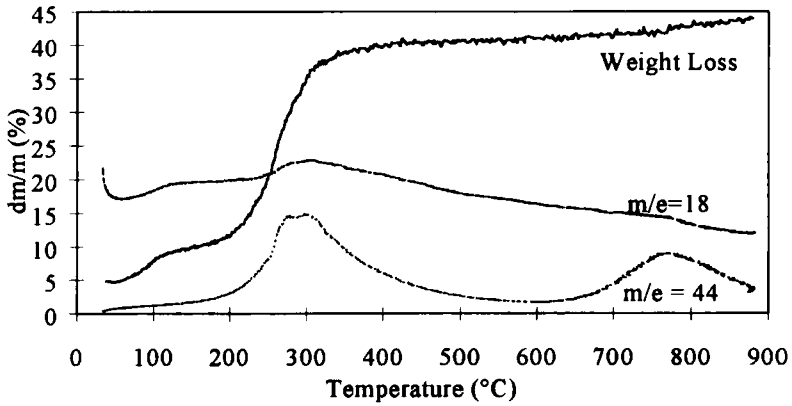

Figure 3 Thermogravimetric analysis of $LaCo(fsa)_2en$-Taen, and mass spectrometry of the evolved gases.

From the thermogravimetric analysis, it can be concluded that the formation of the nanocomposites is almost achieved at 300°C. The destruction of the intercalated complex is accompanied by a strong decrease of the average $d_{001}$ interlayer distance (Table I). Even if the theoretical proportion of oxide in the nanocomposite based on taeniolite is as high as 42%, lines belonging to an oxide phase were not detected in the diffractogram. This is a good proof that the oxide is present as a very dispersed state, probably intercalated between the host layers to form pillars. Another striking feature is the important analogy of the X ray diffractograms of the two kinds of nanocomposites. It means that they are simply differing by the density of pillars.

Table I Basal spacing $d_{001}$ (Å) of $LaCo(fsa)_2en$-Clay compounds as a function of temperature.

| Temperature (°C) | 20 | 325 | 350 | 400 | 415 |
|---|---|---|---|---|---|
| $d_{001}$ $LaCo(fsa)_2en$-Mont (Å) | 22.7 | 15.5 | - | - | 14 |
| $d_{001}$ $LaCo(fsa)_2en$-Taen (Å) | 24.4 / 32 | - | 15.5 | 14.5 | - |

TEM was used to get more information on the local and non-averaged interlamellar spacing, the evolution of the two-dimensionality and the distribution of the oxide phase. At room temperature, the two exchanged samples have a lamellar morphology comparable to a crumpled sheet of paper, with average values of interfringe distance at 21-22Å for $LaCo(fsa)_2en$-Mont and about 22Å $LaCo(fsa)_2en$-Taen.

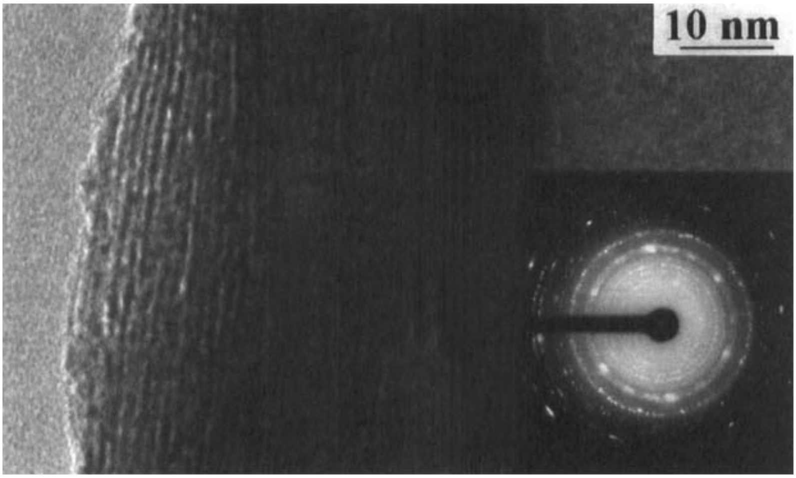

Figure 4 TEM micrograph and SAED of Mont-LaCoO$_y$ at 600°C.

Whatever the pristine silicate, 001 lattice fringes were easily observed even after heating up to 600°C (fig. 4), however numerous defects are always detected. The average interfringe distances are about 15Å (415°C), 14Å (500°C) and 13Å (600°C), for the montmorillonite nanocomposite ; 14Å (400°C) and 13Å at 500°C for the taeniolite nanocomposite.

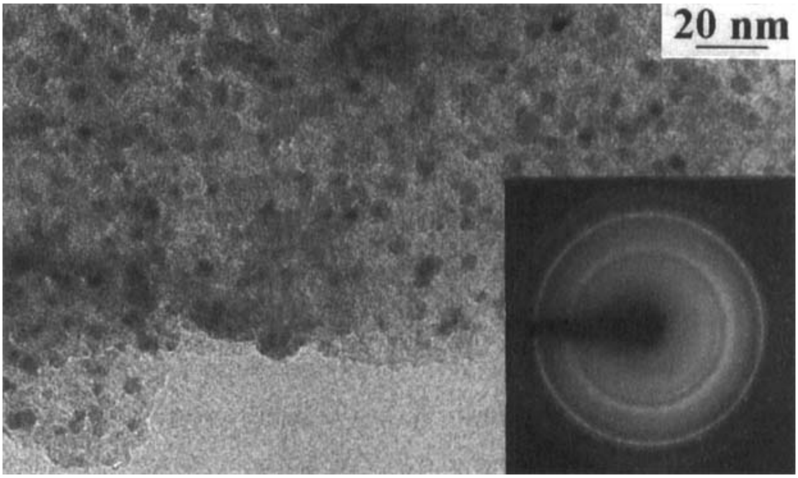

Figure 5 TEM micrograph and SAED of Mont-LaCoO$_y$ at 400°C.

Above 400°C, for both nanocomposites, dark particles appearing on the bright field images are attributed to oxide particles (fig. 5). Their homogeneous, distribution and size, and their absence on the grid film, strongly suggest that they are well distributed within the matrix to form pillars. Upon increasing temperature, the particles diameter increases from 20-40Å at 400°C to 20-250Å at 600°C due to local coalescence. Below 600°C, SAED (selected area electron diffraction) gives mainly rings attributed to the turbostratic host matrix (fig. 4). The very well defined spots appearing at 600°C show the beginning of a sintering process within the clay matrix (fig. 5).

## CONCLUSION

When the intercalated clays are heated, the organometallic interlamellar cation is decomposed above 270°C, leading to the formation of the nanocomposites. A partial deshydroxylation of the smectite layers occurs around 500°C and leads to the progressive damaging of the Mont-$LaCoO_y$ nanocomposite before its sintering at about 600°C. In the case of Taen-$LaCoO_y$, the sintering of the nanocomposite only takes place above 700°C. The better thermal stability of taeniolite due to its different chemical composition (substitution of F atoms to OH groups in the pristine lattice), is responsible for this higher stability of the nanocomposite.

### References

1. Properties and applications of Perovskite-type Oxides (Edited by L.G.Tejuca and J.L.G.Fierro.), p. 271. Marcel Dekker, New York (1992).
2. A.Wold, B.Post and E.Banks, J. Amer. Chem. Soc. **79**, 4911 (1957).
3. J.Tascon., S.Mendioroz and L.Gonzalez Tejuca, Zeit. Ph. Ch. N. Folge **124**, 109 (1981).
4. S.Skaribas, P.Pomonis, and A.Skoudos, J. Mater. Chem. **1**, 781 (1991).
5. S.Moreau, J.Choisnet and F.Beguin, J. Phys. Chem. Solids **57**, 1049 (1996).
6. A.Lavados., P.Pomonis and S.Skaribas, Materials Science Forum **91-93**, 799 (1992).
7. S.Moreau, S.Pessaud and F.Beguin, *Proc. "Scientific Bases for the Preparation of Heterogeneous Catalysts VI"*, (Ed. G. Poncelet et al.), Elsevier, p. 523 (1995).
8. S.Moreau, Ph D Thesis, University of Orléans, France (1996).