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Pharmaceutical silver doped clays: an EXAFS study from silver to silicon K-edges absorption

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Abstract.

The remarkable adsorption properties of the montmorillonite clay are used to elaborate a silver doped clay, intended to a therapeutical application to burns. The unstable properties of the material obtained lead us to examine the localization of the added silver in the clay matrix by EXAFS spectroscopy performed at the Ag and Si K-edge. The results show that Ag atoms formed in triangular clusters are coordinated to the triangular designs of oxygen atoms on the border plane of the layers of the clay. The local negative charge in the border plane explains the reduction of Ag^+ ions, at the origin of the instability observed for this material.

1 - INTRODUCTION.

The remarkable adsorption properties of the montmorillonite clay (smectite group) originate from its structure built of two-dimensional tetrahedral sheets linked by one octahedral sheet, forming a T-O-T layer, the interlayer space presenting various thicknesses. (Fig 1). The SiO_4 tetrahedra share three oxygen corners (the basal oxygens) that form an hexagonal mesh pattern on the border of the T-O-T layer. Isomorphous substitutions of less-charged cations in the $\text{Al}(\text{O},\text{OH})_6$ octahedral sheet produce a resultant negative charge on the layers. Individual or hydrated cations (Na^+ , K^+ , Mg^{2+}) which are present in the interlayer space, balance this apparent negative charge. In the montmorillonite, the low density charge in the layer border plane, and the soft bonding with the interlayer cations explain the possible exchange with other species.

FIG 1 : Atomic structure of a layer of montmorillonite.

The Ag^+ added clay is prepared by contact with a AgNO_3 solution, and the capacity of fixation presents a saturation level of about 7,7mg per gramme of clay.

EXAFS spectroscopy at the Ag and Si K-edge is performed to study the structure of this poorly material.

2 - EXAFS RESULTS.

FIG 2 : Absorption spectrum collected at the Ag K-edge.

Fig 3 : XANES spectra at the Si K-edge.

We have used EXAFS technique at two extremal energy ranges as we need to register X-Ray absorption spectra around Ag K-edge (25520eV) at DCI (storage ring Orsay), and around Si K-edge (1848eV) at Super Aco (Orsay). Thus, the sample preparation was adapted to these hard and soft X-Rays and, the spectra resolution, the various features were observed at different levels.

Concerning the Ag K-edge, the low content (8 mg/g) of silver obliged us to prepare thick pellets (about 1 cm), and the spectra were collected at liquid He temperature to limit the thermal disorder of Ag atoms. The spectra present weak oscillations related to silver dilution. (Fig 2) Because of the weakness of the signal, it was rather difficult to obtain the normalized EXAFS spectra. The interpretation of the radial distribution function in relation with the structural problem investigated was not easy: either the interlayer Ag^+ cations are trapped in the hexagonal cavities in the border plane of the layer, and so are neighbored by one Si atom of the T sheet, or they are bounded in a different configuration to O atoms of the border plane.

Two series of XANES and absorption spectra of samples of pure and Ag^+ -dopped clay are collected at the Si K-edge. The samples of about 1mm thickness are prepared by decantation on a Micropore film. Figure 3 shows that the spectra are quite identical, which rules out the hypothesis of a Ag-Si bounding.

A final treatment of the data lead to a RDF which can be interpreted: a linear model describes the pre-edge background, and the post-edge absorption is reproduced by a fifth degree polynomial function. Fourier transform using an Hamming window on a selected part of the normalized EXAFS spectra ($2.6 < k < 13.6 \text{ \AA}^{-1}$) gives the RDF in figure 4 where the peaks ending to the final fits are indicated.

The fits are obtained using experimental phase and amplitude backscattering functions extracted from Ag₂O and Ag metal reference compounds treated in the same way as the samples studied. Table 1 presents the final parameters obtained, and figure 5 a and b the fits of the two shells identified. They describe the Ag atoms surrounding as made of a first shell of O atoms, and a second one of Ag atoms. The Debye-Waller factors $\Delta\sigma$ are the difference between thermal disorder terms of O and Ag atoms in the crystalline reference compounds and the much less organized doped clay.

FIG 4 : RDF function at the Ag K-edge.
The major peak corresponds
to the Ag atoms second shell.

TABLE 1: Silver surrounding atoms. Parameters obtained from the fits.
N: number of coordination, R: Ag-atom distance, $\Delta\sigma$: Debye-Waller factor.

Sample Ag conc. (mg/g)	1 st shell of Oxygen atoms			2 ^d shell of Ag atoms		
	N	R(Å)	$\Delta\sigma$ (Å)	N	R(Å)	$\Delta\sigma$ (Å)
7.80	0.8 ± 0.3	1.99 ± 0.03	0.07	2.0 ± 0.3	2.86 ± 0.02	0.06
7.66	0.8 ± 0.3	2.01 ± 0.03	0.06	1.9 ± 0.3	2.85 ± 0.02	0.07
7.53	0.75 ± 0.3	2.00 ± 0.03	0.07	1.9 ± 0.3	2.86 ± 0.02	0.06

FIG 5 a : Fit of the first peak
(O atoms shell)

FIG 5 b Fit of the second peak
(Ag atoms shell)

3 - DISCUSSION.

The environment of each silver added atom is made of two silver atoms at a distance of $2,86\text{\AA}$, which is close to the Ag-Ag distance in metal ($2,89\text{\AA}$) and for each one, as a mean, in the order of 0.8 neighbour oxygen atom. These results rule out the formation of silver oxide Ag_2O . The figure which interprets these structural results is an aggregation of the additional silver atoms in triangular clusters. The tendency of Ag^+ cations to form such triangular motifs is known in ternary silver oxides and some other inorganic silver compounds (1,2,3).

On the border plane of the T-O-T layers of the clay, oxygen atoms form a pattern of hexagonal cavities, linked by oxygen triangular figures which are the base of the SiO_4 tetrahedra. Because of the isomorphic substitution of less-charged cations in the octahedra (mainly Mg^{2+} substituted to Al^{3+}), some oxygen atoms bear a partial negative charge which can act as a fixation point of the Ag^+ added cations. According to the localization of these negative charges in the triangular figures of oxygen atoms, one, two, or each of the three atoms of the silver clusters are bounded to oxygen atoms (Fig 6). The total mean number of oxygen neighbours (in the order of 0.8) results from the sum of the mean number of oxygen neighbours for each silver atom ($1/3$, $2/3$, 1), weighted by the occurrence ratio of each of the three configurations, which cannot be estimated by our structural investigation. This accounts for the results of EXAFS analysis: the Ag-Ag distance in the clusters ($2,86\text{\AA}$) is compatible with the O-O distance ($2,60\text{\AA}$) on the basis of the SiO_4 tetrahedra, and the Ag-O distance ($2,00\text{\AA}$) between a silver atom and an oxygen atom of basal plane is close to the Ag-O distance ($2,06\text{\AA}$) in Ag_2O .

Recently, the study of the redox reactions in the photographic process pointed out the fundamental part assumed by the formation of clusters of silver atoms (4). In the photographic emulsion, after the reduction reaction $\text{Ag}^+ + e \Rightarrow \text{Ag}^0$, silver atoms gather and form clusters which are surrounded by Ag^+ ions which form a complex like pair $\text{Ag}^0\text{-Ag}^+$, in which these two atoms share a positive charge. On the border plane of the layers, some oxygen atoms are fixation points, and donors of electrons which lead to the reduction of one, two or three of the bounded Ag^+ ions of the clusters, which then contain either the two species Ag^0/Ag^+ , or only Ag^0 atoms.

Our model of Ag clusters in the clay is obtained from experimental data collected at 4.2 K, because the high thermal disorder of Ag atoms prevents to register a good quality absorption spectra at RT. However our model can be extrapolated at RT where the existence of such clusters in a higher thermal energy state is demonstrated in the photographic process previously referenced.

According to this model, the formation of metallic silver clusters results from the interaction of Ag^+ ions with the clay which acts like a donor of electron medium. (The high Debye-Waller factor of oxygen surrounding atoms (Table 1) indicates a soft bounding between the clusters and the border plane). This description explains the blackening of the silver added clay and the difficulty to extract further a regular concentration of the Ag^+ ions trapped in the clusters.

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Fig 6 : Localization of the triangular silver-clusters on the border plane of O atoms of the layers of the montmorillonite. One, two, or three atoms of the clusters are bounded to one, two, or three of the O atoms of the base of the SiO_4 tetrahedra.