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► **To cite this version:**

E. Montarges, L. Michot, Ph. Ildefonse. Structural Studies of Hydroxy-Ga Pillared Clays by Ga K-Edge X-Ray Absorption. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-829-C2-830. 10.1051/jp4:1997251 . jpa-00255330

**HAL Id: jpa-00255330**

**<https://hal.science/jpa-00255330>**

Submitted on 4 Feb 2008

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## Structural Studies of Hydroxy-Ga Pillared Clays by Ga K-Edge X-Ray Absorption

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**Abstract.** A natural montmorillonite clay was intercalated by hydroxy-Ga polycations ( $\text{Ga}_{13}$ ), obtained by basis hydrolysis of metal salts. These species are structural analogues of  $\text{Al}_{13}$ . The clay interlayer cations were exchanged in  $\text{Ga}_{13}$  solutions containing various amounts of organic polymer. The synthesized materials were aged and/or calcined to 150 and 500°C. In a first approach, Ga-K edge experiments were carried out to investigate the local environment of Ga atoms intercalated into the interlayer space. The study of the first nearest neighbours, oxygen atoms, revealed a decrease in the average bond distance after calcination, which traduced dehydroxylation of the  $\text{Ga}_{13}$  pillars. By studying the second nearest neighbours, gallium atoms, the Fourier transforms indicate the presence of the central tetrahedrally coordinated gallium of the  $\text{Ga}_{13}$  polycations whose contribution disappears upon ageing or calcination.

### 1. INTRODUCTION

Metal oxide pillared clays, obtained by exchange reactions of smectite with polycations, can be used as catalysts or adsorbents. The most commonly used pillaring agent is the Keggin-like  $\text{Al}_{13}$  oligomer  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24+x}(\text{H}_2\text{O})_{12-x}]^{(7-x)+}$ , made from twelve octahedra surrounding a central aluminum tetrahedron (1, 2).

In order to improve the adsorption capacities of aluminum pillared clays, we have tried to modify the synthesis procedure by adding an organic polymer in the pillaring solution (3). The different resulting materials were aged or calcined at 500°C. X-ray diffraction patterns revealed that: (i) cointercalation of polymer improves the hydrolytic stability of  $\text{Al}_{13}$  polycations; (ii) this procedure results in a shift towards lower basal spacings after calcination at 500°C.

Taking advantage of the structural analogy between Ga salts obtained by hydrolysis of gallium chloride and  $\text{Al}_{13}$  polycations (4), the local structure of these materials can be approached by X-ray absorption experiments carried out at the Ga-K edge on gallium pillared clay samples.

### 2. MATERIALS

#### 2.1 Smectites

The clay used in this study was a natural Wyoming montmorillonite purchased from the Source Clays Mineral Repository at the University of Missouri, Columbia MO and is referred to as SW in this text. The unit cell formula is  $(\text{Si}_{7.96}\text{Al}_{0.04})(\text{Al}_{3.12}\text{Mg}_{0.45}\text{Fe}^{\text{II}}_{0.16}\text{Fe}^{\text{III}}_{0.27})\text{O}_{20}(\text{OH})_4(\text{Na}^+)_{0.65}$  and the cation exchange capacity is 85 meq/100g.

#### 2.2 Pillaring solutions

$\text{Ga}_{13}$  solution was prepared by adding dropwise a 0.4 M solution of sodium hydroxide to a 0.2 M solution of gallium chloride in order to obtain a final hydrolysis ratio  $\text{OH}/\text{Ga} = 2.0$ . The polymer is a polyethyleneoxide (PEO) of 100 000 g/mole molar weight. 300 ml of a PEO solution was added to a 120 ml aliquot of the fresh  $\text{Ga}_{13}$  solution. The different ratios used for the pillaring solutions are described in EO units per mole of  $\text{Ga}_{13}$  and are: 5, 20 and 100.

#### 2.3. Intercalation

The intercalation and calcination procedures are classical and were described elsewhere (3).

### 3. EXAFS SPECTROSCOPY

X-ray absorption spectra around the Ga-K absorption edge (10367 eV) were recorded in transmission using synchrotron light from the DCI storage ring of the LURE-Orsay radiation center (France). Energy selection was made using double-crystal monochromator with two Si(311) crystals. Ge K-edge (11106 eV) was used for calibration. Energy was scanned with 2eV steps from 10250 to 11240 eV. For each sample three spectra were collected and added. EXAFS data were deduced using a standard procedure (5) with Michalowicz programs. Interatomic distances were calculated using Feff theoretical phase shift and amplitude functions (6). Synthetic  $\text{GaOOH}$  was used as a reference for analysing Ga-O contributions and for extracting  $\gamma$  and  $\Delta E$  values, fixed at  $0.5984 \text{ \AA}^{-2}$  and 2.0707 eV respectively for the first shell. For the second shell, Ga-Ga bondings,  $\gamma$  and  $\Delta E$  values were extracted from the simulation of  $\text{Ga}_{13}$ -montmorillonite EXAFS oscillations and fixed to  $0.736 \text{ \AA}^{-2}$  and 4.1823 eV respectively.

### 4. RESULTS AND DISCUSSION

#### 4.1 First nearest neighbours

The distance values of Ga-O (1.92 and 2.05 Å) in  $\text{GaOOH}$  were obtained from literature data (7). Table 1 presents the values obtained by simulation with Feff theoretical files.

sample	N	$\sigma$ (Å)	R (Å)	sample	N	$\sigma$ (Å)	R (Å)
SW+Ga <sub>13</sub>	4	0.06	1.92	SW+Ga <sub>13</sub> +PEO (20u/Ga <sub>13</sub> )	4	0.06	1.94
	2	0.05	2.04		2	0.06	2.05
SW+Ga <sub>13</sub> calcined at 500°C	4	0.08	1.88	SW+Ga <sub>13</sub> +PEO (20u/Ga <sub>13</sub> ) calcined at 500°C	4	0.09	1.88
	2	0.10	2.04		2	0.11	2.02
SW+Ga <sub>13</sub> aged 7 months	4	0.07	1.92	SW+Ga <sub>13</sub> +PEO (20u/Ga <sub>13</sub> ) aged 7 months	4	0.07	1.94
	2	0.08	2.04		2	0.07	2.05

Table1 : N number of neighbour,  $\sigma$  Debye-Waller factor,  $\gamma = k/\lambda$ ,  $\lambda$  electron mean free path, R Ga-O atom distance,

The contribution of oxygen atoms neighbours to the EXAFS signal was interpreted as the sum of Ga<sup>VI</sup>-OH (short bond lengths) to Ga<sup>VI</sup>-OH<sub>2</sub> and to Ga<sup>VI</sup>-O-Ga<sup>IV</sup> (large bond lengths) contributions. The simulation was carried out with two shells, respectively constituted of four and two oxygen atoms neighbours.

After calcination, the Ga-OH distances decreased, due to the dehydroxylation of the polycation. Seven months ageing of the Ga<sub>13</sub> intercalated montmorillonite results in no change in the bond distances.

#### 4.2 Second nearest neighbours

Figure 1 presents the Fourier transforms corresponding to the Ga-Ga contribution to EXAFS oscillations. Fresh samples Fourier transforms (curves a and b) exhibit two peaks. The main peak is attributed to edge-sharing Ga<sup>VI</sup> - Ga<sup>VI</sup> bondings ( $R = 3.03 \pm 0.02$  Å), the right peak can be assigned to the presence of central tetrahedrally coordinated gallium atom ( $R=3.53 \pm 0.03$  Å), based on Al<sub>13</sub> crystallographical data (2).

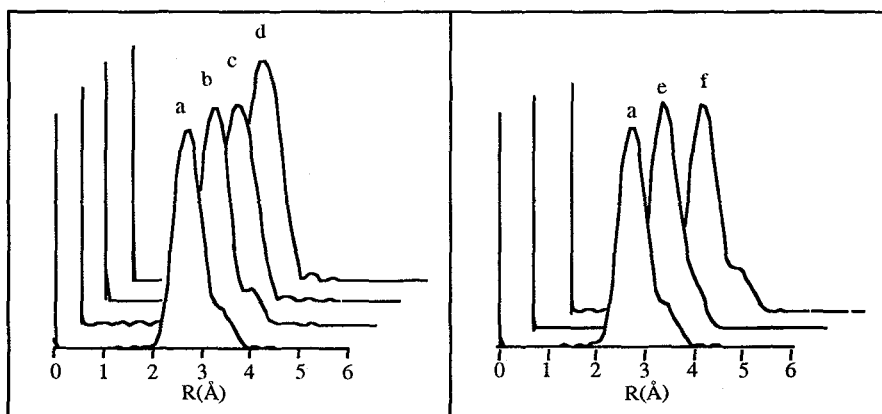


Figure 1 : Fourier transforms after Fourier filtration of Ga-Ga contribution; a : SW+Ga<sub>13</sub>; b : SW+Ga<sub>13</sub>+PEO 20u/Ga<sub>13</sub>; c : SW+Ga<sub>13</sub> calcined at 500°C; d : SW+Ga<sub>13</sub>+PEO 20u/Ga<sub>13</sub> calcined at 500°C; e : SW+Ga<sub>13</sub> aged seven months; f : SW+Ga<sub>13</sub>+PEO 20u/Ga<sub>13</sub> aged seven months.

After calcination, the contribution of central tetrahedral gallium disappears (curves c and d) and the spectra can be simulated using a single neighbours layer, corresponding to Ga<sup>VI</sup> - Ga<sup>VI</sup> bondings. The local structure is not conserved by the presence of polymer in the pillaring solution.

Ageing of the Ga<sub>13</sub> clay (curve e) modifies the structure of the polycation as the number of Ga<sup>IV</sup> neighbours decreases. This evolution, related by a reduction of the shoulder (curve e) is fully prevented when PEO is cointercalated (curve f).

#### Acknowledgements

The authors wish to acknowledge the staff at LURE for the help they provided for the experiments.

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