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EXAFS OF CALCIUM IN OVERBASED MICELLES

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1 - INTRODUCTION

Overbased calcium salts have a wide range of applications, especially as anti-corrosive and anti-wear additives in lubricants, and catalysts in combustion processes. The most popular ones are calcium alkyl benzene sulfonate (ABS) salts which are used in engine oils.

Overbased calcium (ABS) salts are constituted of calcium carbonate colloidal particles (core diameter 20-100 Å depending on the preparation), which are surrounded by a shell of ABS amphiphilic molecules. The CaCO₃ core gives the basicity expressed by the total basic number (TBN), the shell is responsible for the good dispersion and the stability. The synthesis of overbased calcium salts is very complex, with a three phases system, for example: calcium oxide as a solid, ABS acid as a liquid and carbon dioxide as a gas. Furthermore, promotors and other ingredients are necessary to obtain the final product.

As it is thought that this reaction takes place in a micellar phase, such CaCO₃ particles are often called "micelles", although it seems that they have no critical micellar concentration (CMC).

From previous works [1] it appears that the microstructure of the CaCO₃ core is determinant to explain both mechanisms of preparation and anti-wear effect. High Resolution Transmission Electron Microscopy (HRTEM) shows the amorphous character of the calcium carbonate core when such particles are deposited on a thin carbon film (figure 1).

The present paper reports EXAFS data recorded at the calcium K-edge of an overbased ABS salt.

Figure 1: HRTEM image of one calcium carbonate micelle deposited on a carbon grid, showing the structureless feature of the core.
2 - EXPERIMENTAL PROCEDURE

Calcite was used as a standard in order to study the amorphous system, moreover calcite was obtained in a colloidal form by the cristallisation of amorphous carbonate micelles in the same paraffinic medium.

The specimens are centrifugated at 3000 g to eliminate large paticles and dusts till they are optically clear. The experiments were performed on the EXAFS 3 spectrometer (LURE/DC1), the ring running at 1.85 Gev.

3 - RESULTS

The EXAFS of calcium in calcite is shown in figure 2a, the results of the treatment is shown in figure 2b (both modulus and imaginary part of the TF of calcium are shown).

The crystal structure of calcite is well established, it has a trigonal structure, the calcium ions and the carbon atoms of the carbonate ions all lie on the trigonal \((Z)\) axis), and the orientations of the two coplanar carbonate ions are staggered relative to each other so that there is a centre of symmetry in the unit cell. The first shell consists of 6.0 atoms of oxygen at 2.35 \(\text{Å}\) and the forth shell consists of 6.0 atoms of calcium at 4.04 \(\text{Å}\). Considering these facts, we can state the following points:

- the strong peak in the XANES at 20 eV past the edge is related to the colinearity of calcium and carbon atoms. Previous works showed that it does not exist in aragonite [2],

\begin{center}
\textbf{Figure 2 : Data on crystallized calcite (CaCO3)}
\end{center}

\begin{itemize}
  \item 2a : K-edge of Calcium
  \item 2b : RDF of calcium (modulus and imaginary part of the TF)
\end{itemize}
as expected, the calcium RDF shows two contributions, the Ca-0 distance at 1.74 Å, and the Ca-Ca distance at 3.51 Å (no phase shift corrected distances). It is known that calcium EXAFS is relatively poor but the consideration of both EXAFS and XANES seems very useful in our case.

The calcium K-edge of the micellar form is presented in figure 3a. From a rough examination of the two spectra figure 3a and figure 2a, it appears that both XANES and EXAFS are affected by the structural change. Compared to the case of crystallized CaCO3 (calcite), the following points can be highlighted considering the micellar form:
- there is only one distribution in the EXAFS modulations, indicating the amorphous character of the micellar core,
- the strong peak at 20 eV past the edge does not appear.

Therefore, structural information on calcium environment is contained in the spectra. The following one only concerns the treatment of the EXAFS part (from 50 eV past the edge). The RDF of calcium (figure 3b) clearly shows a single distance at 2.38 Å (phase shift corrected) corresponding to the Ca-0 bond and a decrease of the amplitude compared to the case of calcite (figure 2b). This could be attributed to two reasons:
- a decrease in the number of coordination,
- an increase of the disorder in the oxygen coordination sphere (Debye Waller factor $\sigma > 0$).

To study these two hypothesis, fitting curves were obtained with different values of $N$ and $\sigma$, keeping the Ca-0 distance at the same average value. Results show (figure 4), that the best fit is obtained with 7.5 atoms at 2.38 Å, with $\sigma$ equal to 0.22.

**Figure 3:** Data on micellar CaCO3

3a : K-edge of calcium
3b : RDF of calcium
4 - CONCLUSIONS

By comparison of the EXAFS of calcium K-edge in two different calcium carbonate microstructures (respectively crystallized calcite and an a micellar form), the following facts have been established concerning the micellar form:
- calcium carbonate has a highly amorphous character,
- the coordination number of the Ca-O bond is changed and seems to be higher than in calcite; this latter point can be explained by the effect of the disorder,
- the strong peak at 20 eV past the edge attributed the colinearity between Ca and C atoms in calcite, is absent in the micellar form.

To conclude, it is suggested that calcium carbonate in overbased ABS calcium salts has a high disordered microstructure. Further studies of calcium XANES are now planned in the future.

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