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Molecular orientation of molybdate ions adsorbed on goethite nanoparticles revealed by polarized in situ ATR-IR spectroscopy

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ABSTRACT

The speciation of species adsorbed on nanoparticles is a major concern for several fields, as environmental pollution and remediation, surface functionalization, or catalysis. Attenuated total reflectance infrared spectroscopy (ATR-IR) was amongst the rare methods able to give in situ information about the geometry of surface complexes on nanoparticles. A new possibility using this technique is illustrated here with the MoO_4^{2-}/goethite system. Using deuterated goethite to avoid spectral interferences, adsorption of molybdate ions on a spontaneous oriented film of nanoparticles has been followed using a polarized infrared beam. From the decomposition of spectra in the x, y and z directions, a monodentate surface complex on the {101} faces has been found as the most probable geometry. This result demonstrates that polarized ATR-IR allows to characterize in more details adsorption mode at the atomic scale, in comparison with usual ATR-IR spectroscopy.

1. Introduction

Attenuated total Reflectance infrared spectroscopy (ATR-IR) has become one of the most promising tools to decipher the geometry of surface complexes formed after the adsorption of organic or inorganic species onto nanoparticles [1,2]. Its unique ability to obtain spectra of low adsorbate concentration in presence of solution allows obtaining a picture of the real system, without disturbance, as drying, or modification, as the increase of adsorbate concentration to enhance the signal. The information given by this method is at the same spatial scale as recent surface complexation models as MUSIC [3]. Moreover, recent numerical simulations are able to predict infrared absorption spectra of adsorbed species, with an unprecedented accuracy for frequencies [4]. Thus, raw results obtained by ATR-IR spectroscopy and their interpretation are important data expected by a large community of researchers working on the improvement of the modelling of oxide/water interfaces.

From the original work of Hug [5] who pioneered the use of ATR-IR to obtain information about the geometry of surface complexes onto oxides particles, the protocols have slightly evolved. Some works have shown the interest for the study of kinetics of phenomena [6], others were focused on the spectra treatment to improve the interpretation using 2D-correlation for example [7]. However, the more promising evolution is that based on the use of polarized beam, which allows to go further in the geometry determination of the adsorbate. In literature, the use of polarized beam in ATR geometry has been restricted to two

main domains: (1) determine the orientation of particles [8], or (2) obtain information on species directly adsorbed on the ATR element [9]. However, Wang and Wang [10] have demonstrated, using an anionic exchanger (layered double hydroxide) with a platelet geometry forming a oriented layer on the ATR crystal, that it is possible to get polarized spectra of nitrate ions inside the particles, and so, to deduce the orientation of nitrate ions in the interlayer. LDH have a huge sorption capacity, in comparison with oxides particles, due to the different sorption mechanism (exchange vs. adsorption). Thus, the same experiments with oxides nanoparticles have not been performed, and, to the best of our knowledge, and a protocol to obtain the geometry of surface complex from polarized ATR-IR is still to be developed.

In this work, we have studied the sorption of molybdate ions onto goethite particles, deposited on ATR crystal in an oriented way. In our previous works, adsorbed molybdate species have been characterized by ATR-IR on several substrates (layered double hydroxide [11] and iron (hydr)oxides [12]). Polarized ATR-IR has been used to determine the orientation of particles, and then, to conclude on the reactive faces of the goethite nanoparticles, and the geometry of the surface complex. Deuterated goethite has been synthesized to avoid the interferences between solid and molybdate vibration modes.

2. Material and methods

2.1. Chemicals

All solutions and suspensions in aqueous phase were prepared using purified water (Milli-Q, Millipore) with a resistivity of 18.2 MΩ·cm. An aqueous molybdate solution (0.1 M) was prepared from Na_2MoO_4,

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$2H_2O$ (Prolabo). In sample solutions, the ionic strength was fixed to 0.01 M using NaCl salt (Prolabo). Acidification was performed with a 0.1 M HCl solution (from VWR BDH Prolabo). A deuterated goethite (α-FeOOD) was synthesized according to the protocol given by Cole et al. [13]. α-FeOOH nanoparticles were synthezised according to Lemaire et al. [14].

2.2. Polarized ATR-IR spectroscopy

The experimental setups are similar to those described in our previous studies [11,12]. The ATR-FTIR spectra were collected with a dry-air-purged Thermo Scientific Nicolet 6700 FT-IR equipped with a MCT detector. Spectral resolution was 4 cm^{-1} and spectra were averaged from 256 scans. The horizontal ZnSe crystal with a single reflection (A = 2.54 mm^2) and an angle of incidence of 45° (Smart PIKE) was coated with 1 μL of the goethite suspension (1 g/L) which was dried under a flow of N_2. This procedure was repeated three times. The flow cell was placed on the ATR accessory and a background recorded when the initial solution (0.01 M NaCl) reached the oxide film for conditioning, with a constant velocity of 1 mL/min using a peristaltic pump (Ismatec S.A.) at room temperature. After at least two hours of stabilization, the background spectrum was recorded and a given volume of a 0.1 M sodium molybdate solution stock was subsequently added to the circulating solution. For data reprocessing OMNIC software was used and spectra were decomposed with Gaussians peaks and linear baseline made by interpolation using OriginPro 8.6 software. To collect polarized ATR-FTIR spectra, a ZnSe manual polarizer (Pike Technologies) was placed between the light source and the ATR accessory to select the polarization of the IR beam. Two spectra have been collected, corresponding to either p-polarized light or s-polarized light (A_p and A_s spectra respectively). Polarized spectra along the Cartesian directions (A_x, A_y and A_z) has been calculated using the following equations, with k = 0.791 for our set-up [15,16]:

$$A_x = k \cdot A_s \tag{1a}$$

$$A_y = A_s \tag{1b}$$

$$A_z = A_p - k \cdot A_s \tag{1c}$$

A calibration has been made on an ideal isotrotropic sample (a 0.1 M HNO_3 solution has been chosen). Thus, A_z/A_x, A_z/A_y and A_y/A_x calculated for HNO_3 solution have been found equal to 1.17, 0.93 and 1.26,

respectively. The slight differences with the expected value of 1 comes from the polarizer itself, and the values calculated from Eqs. (1a), (1b), and (1c) for adsorbed molybdate species have been normalized by dividing the ratios by the values listed above.

3. Results and discussion

The morphology of particles has been investigated using Scanning Electron Microscopy (SEM) (Fig. 1A) to get the picture of the powder dispersed on a conductive adhesive carbon tape. A typical acicular shape has been found, as previously observed on protonated goethite [17]. The profiles are consistent with the interpretation given for goethite [17] where authors concluded on particles lying on {001} faces with {101} lateral faces from Atomic Force Microscopy pictures, using a $Pnma$ space group. The first step of our protocol is to check that an orientated layer was spontaneously formed on the ATR crystal, and to determine the orientation of the particles.

ATR-IR spectra of α-FeOOH and α-FeOOD are shown in Fig. 1B. Protonated goethite is characterized by bands at 893 and 792 cm^{-1}, assigned to coupled δ and γ vibration modes [18]. For deuterated goethite, these bands are shifted to lower wavenumbers and the δ mode is located at 697 cm^{-1}. Two small peaks are visible at 944 and 895 cm^{-1}, respectively assigned to uncoupled δOH and a residual coupled δOH. Band at 2373 and 2341 cm^{-1} are assigned to OD stretching vibrations, corresponding to the OH stretching vibrations around 3128 cm^{-1} in protonated goethite.

These vibrations can be used to determine the orientation of particles after the deposition of a thin layer since they correspond to stretching of bonds in given directions. Thus, bands at 944 and 895 cm^{-1} are assigned to transition dipole moment in the (001) plane, due to Fe-O-D bending [18]. They are visible only in the spectra polarized in x and y directions (Fig. 2A), this can lead to the conclusion that {001} faces are parallel to the ATR element. OD stretching vibrations are located around 2350 cm^{-1}, corresponding to bands visible around 3100 cm^{-1} in protonated goethite. Following the work by Williams and Guenther [19], the higher frequency vibration (2341 cm^{-1} here) has been assigned to a stretching mode with transition dipole moment in the (100) direction. It is present in spectra polarized in x and y directions, indicating that particles form a layer with their {001} faces parallel to the ATR element, but randomly orientated in x and y directions. Moreover, the band at 2373 cm^{-1} has been assigned to a stretching mode with transition dipole moment in the (001) direction [19], and is present only in the spectra polarized in z direction, confirming that {001} faces are parallel to the
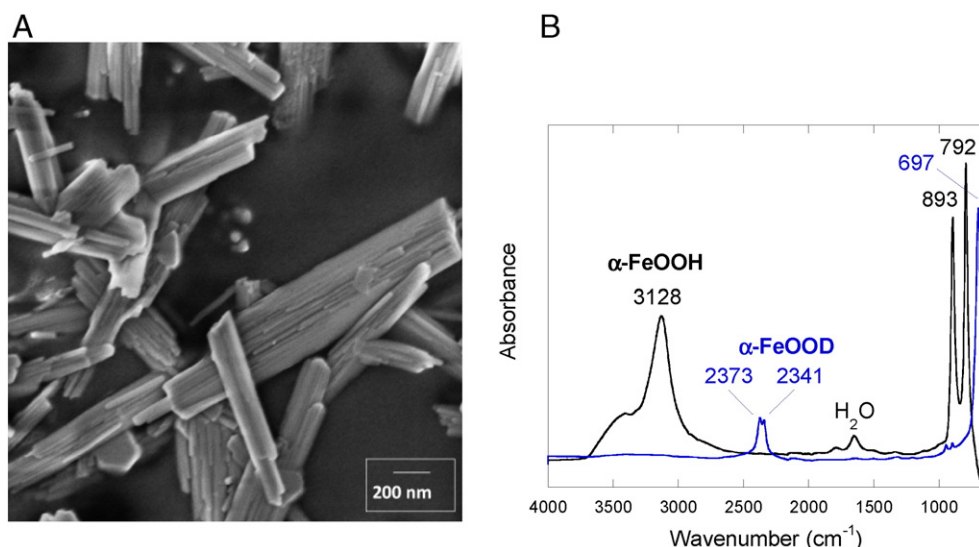

Fig. 1. (A) SEM picture of α-FeOOD. (B) ATR-IR spectra of layers of α-FeOOH and α-FeOOD.