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Interaction Mechanisms between Uranium(VI) and Rutile Titanium Dioxide: From Single Crystal to Powder

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This paper is devoted to the study of the mechanisms of interaction between uranyl ion and rutile TiO_2. Among the radionuclides of interest, U(VI) can be considered as a model of the radionuclides oxo-cations. The substrate under study here is the rutile titanium dioxide (TiO_2) which is an interesting candidate as a methodological solid since it can be easily found as powder and as manufactured single crystals. This material presents also a wide domain of stability as a function of pH. Then, it allows the study of the retention processes on well-defined crystallographic planes, which can lead to a better understanding of the surface reaction mechanisms. Moreover, it is well-established that the (110) crystallographic orientation is dominating the surface chemistry of the rutile powder. Therefore, the spectroscopic results obtained for the U(VI)/rutile (110) system and other relevant crystallographic orientations were used to have some insight on the nature of the uranium surface complexes formed on rutile powder. This goal was achieved by using time-resolved laser-induced fluorescence spectroscopy (TRLFS) which allows the investigation, at a molecular scale, of the nature of the reactive surface sites as well as the surface species. For rutile surfaces, oxygen atoms can be 3-fold, 2-fold (bridging oxygens), or single-fold (top oxygens) coordinated to titanium atoms. However, among these three types of surface oxygen atoms, the 3-fold coordinated ones are not reactive toward water molecules or aqueous metallic cations. This study led to conclude on the presence of two uranium(VI) surface complexes: the first one corresponds to the sorption of aquo UO_2^{2+} ion sorbed on two bridging oxygen atoms, while the second one, which is favored at higher surface coverages, corresponds to the retention of UO_2^{2+} by one bridging and one top oxygen atom. Thus, the approach presented in this paper allows the establishment of experimental constraints that have to be taken into account in the modeling of the sorption mechanisms.

Introduction

In the fields of nuclear waste storage and of uranium contaminated areas (mining and reprocessing), the assessment of water contamination, depending on the retention/migration of heavy metal ions in the ground, is of primary environmental concern. The prediction of the ion migration requires details on the mobility and chemical behavior of these ions in the geological environment.[1,2] Among the various physicochemical reactions involved especially in contaminant transport in groundwater[3−6] and water treatment,[7] the sorption of heavy metal ions at the solid/water interface are the most important processes. Therefore, metal sorption onto transportable or nontransportable mineral surfaces has to be accurately quantified. However, this quantitative description depends on several different geological parameters, such as, for instance, pH, redox potential, and ionic strength of the aqueous phase and reactivity of the mineral substrates. To date, a lot of radionuclides sorption experimental data are available, which have been mainly modeled with either distribution coefficients or thermodynamic model (ion ex-

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(1) Morrison, S. J.; Tripathi, V. S.; Spangler, R. R. *J. Contam. Hydrol.* **1995**, *17*, 347.
(2) Arnold, T.; Zorn, T.; Bernhardt, G.; Nitsche, H. *Chem. Geol.* **1998**, *151*, 129.
(3) Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1989.
(4) Davis, J. A.; Kent, D. B. In *Reviews in Mineralogy: Mineral water interface Geochemistry*; Hochella, M., Jr., White, A., Eds.; Mineralogical Society of America: Washington, 1990; Vol. 23(5), p 177.
(5) Stumm, W. *Chemistry of the Solid-Water Interface*; J. Wiley & Sons: New York, 1992.
(6) Guillaumont, R. *Radiochim. Acta* **1994**, *66/67*, 231.
(7) Browski, A. *Adv. Colloid Interface Sci.* **2001**, *93*, 135.

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change, surface complexation)[8−13] but without any accurate characterization of the nature and the structure of the sorbed species as well as the surface reactive sites of the minerals. Often, such a macroscopic approach gives, indeed, model dependent thermodynamic constants without general applicability. Therefore, over the past few years, some microscopic structural investigations of the interface have been performed.[14−17] Nevertheless, only a few studies have modeled retention data taking into account the results obtained using the microscopic spectroscopic approach.[18−21]

While, following this methodology, the substrates investigated were mainly powders of phosphate and oxide solids and also of clays, it is proposed in this paper to carry out this kind of structural study on single crystals. This will allow one a better understanding, at a molecular scale, of the interaction mechanisms between the metal ion and the surface. The solid chosen here is the rutile titanium dioxide, which was studied under both powdered and single crystal forms. Three crystallographic orientations were considered: (110), (001), and (111). Since this oxide has important application in catalysis and photocatalysis, its surfaces have been the subject of many studies.[22−27] Moreover, because of its high stability over a wide range of pH values, it is used as a model mineral. In particular, TiO_2 (110) is the most stable face because the titanium atoms of this surface have the largest coordination number of the low-index surfaces[28−30] which explains that the rutile powder is mainly made up of the (110) plane.[31,32] Despite these very particular properties, the sorption of very few actinides has been studied, up to now, with this oxide,[33] and then the structural investigation of the interactions between the hexavalent uranium ion and TiO_2 surface was shown to be particularly pertinent.

The spectroscopic technique used in this work is the time-resolved laser fluorescence spectroscopy (TRLFS). This method will supply information on the structure of the uranium environment, such as the number and the nature of the TiO_2 surface reactive sites and the number and the nature of the sorbed uranyl species. Moreover, the results will be compared to those obtained on the U(VI)/TiO_2 powder system, with the same experimental technique. Considering that the powder is, in that case, mainly composed of a limited number of crystallographic planes, it seems interesting to check whether the uranium retention data obtained on the powder could be structurally and quantitatively related to those obtained on the single crystals. Both studies will lead to a better understanding of the surface interactions and will then allow an accurate modeling of these experimental data with only a few adjustable parameters. To our best knowledge, it is the first time that such a comparison with actinide ions has been performed.

Experimental Section

Materials. The titanium dioxide single crystals were purchased from Cerac and were used without any further treatment. Each crystal was 10 × 10 mm and 1 mm thick with two polished faces, and the (110), (111), and (001) crystallographic orientations were considered. Rutile powder was also purchased from Cerac. The powdered substrate was thoroughly washed with deionized water until the pH and the conductivity of the supernatant kept constant. In order to verify that the powder was single phase, XRD measurements were performed with a Bruker D8 Advance. Moreover, the specific surface area of powders was determined using a Coulter SA3100 apparatus with the N_2-BET method (5 points). Uranium(VI) stock solution was prepared by dissolving a known amount of $UO_2(NO_3)_2{\cdot}6H_2O$ (Merck) in an acidified $NaClO_4$ 0.1 M solution (pH = 2) in order to avoid uranium hydrolysis. The concentration of this stock solution was $2.5{\cdot}10^{-2}$ M, determined by α-liquid scintillation counting using a Tri-Carb spectrometer supplied by Packard and the Alphaex cocktail according to the protocol already described in the literature.[34]

Sorption Experiments. The general protocol considered in this work was to perform the batch experiments in two steps, at constant temperature (298 K). First, the solids were hydrated for 12 h, under continuous stirring, in a $NaClO_4$ 0.1 M solution adjusted at the desired pH value. Then, a negligible volume of the uranium(VI) stock solution was added to the suspension, and after 12 h the final uranium concentration as well as the equilibrium pH values were determined. Previous experiments have shown that, after 12 h, both hydration and sorption equilibria were reached. All experiments were performed in polypropylene tubes since preliminary experiments have shown that uranyl ion sorption onto the tube walls was negligible. The partial pressure of carbon dioxide was not controlled since the pH range investigated was from 1.5 to 4.5 and no uranyl carbonate species could be formed in solution for these pH values.

For powders, 200 mg of solid was added to 10 mL of the background electrolyte ($NaClO_4$ 0.1 M, adjusted pH), and the

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(8) Missana, T.; Garcia-Gutierrez, M.; Maffiotte, C. *J. Colloid Interface Sci.* **2002**, *260*, 291.
(9) Li, W.; Tao, Z. *J. Colloid Interface Sci.* **2003**, *267*, 25.
(10) Tao, Z.; Li, W.; Zhang, F.; Ding, Y.; Yu, Z. *J. Colloid Interface Sci.* **2002**, *265*, 221.
(11) Nagasaki, S.; Tanaka, S.; Suzuki, A. *Colloids Surf., A* **1999**, *155*, 137.
(12) Lu, N.; Mason, C. *Appl. Geochem.* **2001**, *16*, 1653.
(13) Degueldre, C.; Wernli, B. *J. Environ. Radioact.* **1993**, *20*, 151.
(14) Takahashi, Y.; Kimura, T.; Kato, Y.; Minai, Y.; Tominaga, T. *Radiochim. Acta* **1998**, *82*, 227.
(15) Stumpf, Th.; Bauer, A.; Choppin, F.; Fanghänel, Th.; Kim, J. I. *Radiochim. Acta* **2002**, *90*, 345.
(16) Ostergren, J.; Bargar, J.; Brown, G.; Parks, G. *J. Synchrotron Radiat.* **1999**, *6*, 645.
(17) Gabriel, U.; Charlet, L.; Schläpfer, C. W.; Vial, J. C.; Brachmann, A.; Geipel, G. *J. Colloid Interface Sci.* **2001**, *239*, 358.
(18) Drot, R.; Simoni, E. *Langmuir* **1999**, *15*, 4820.
(19) Lomenech, C.; Drot, R.; Simoni, E. *Radiochim. Acta* **2003**, *91*, 453.
(20) Ordoñez-Regil, E.; Drot, R.; Simoni, E. *J. Colloid Interface Sci.* **2003**, *263*, 391.
(21) Kowal-Fouchard, A.; Drot, R.; Simoni, E.; Ehrhardt, J. J. *Environ. Sci. Technol.* **2004**, *38*, 1399.
(22) Henrich, V. E.; Cox, P. A. *The Surface Science of Metal Oxides*; Cambridge University Press: Cambridge, 1994.
(23) Williams, C. C.; Ekerdt, J. G.; Jehng, J.-M.; Hardcastle, F. D.; Wachs, I. E. *J. Phys. Chem.* **1991**, *95*, 8791.
(24) Parfitt, G. D. *Croat. Chem.* **1973**, *45*, 189.
(25) Murray, P. W.; Condon, N. G.; Thornton, G. *Phys. Rev. B* **1995**, *51*, 10989.
(26) Onishi, H.; Iwasawa, Y. *Phys. Rev. Lett.* **1996**, *76*, 791.
(27) Diebold, U. *Surf. Sci. Rep.* 2003, *48*, 53.
(28) Onishi, H.; Iwasawa, Y. *Chem. Phys. Lett.* **1994**, *226*, 111.
(29) Lindan, P. J. D.; Harrison, N. M.; Gillan, M. J. *Phys. Rev. Lett.* **1998**, *80−4*, 762.
(30) Novak, D.; Garfunkel, E.; Gustafsson, T. *Phys. Rev. B* **1994**, *50−7*, 5000.
(31) *Rutley's Elements of Mineralogy*, 27th ed.; Unwin Hyman: London, 1988.
(32) Primet, M.; Pichat, P.; Mathieu, M-V. *J. Phys. Chem.* **1971**, *75*, 1216.
(33) Olsson, M.; Jakobson, A. M.; Albinson, Y. *J. Colloid Interface Sci.* **2003**, *266*, 269.
(34) Dacheux, N.; Aupiais, J. *Anal. Chem.* **1997**, *69*, 2275.

Table 1. Summary of the Experimental Conditions for Sorption of Uranyl on Rutile Powders and Codification of the Samples[a]

sample label	$[UO_2^{2+}]_{initial}$ ($mol \cdot L^{-1}$)	pH	sorption rate (%)
RP20	10^{-4}	<3.1	<20
RP25	10^{-4}	3.1	25
RP50	10^{-4}	3.6	50
RP75	10^{-4}	4.0	75
RP90	10^{-4}	4.5	90
RP100	10^{-4}	5.4	100

[a] The ionic strength was 10^{-1} M fixed with $NaClO_4$.

Table 2. Characteristics and Codification of the Main Experimental Samples of Titania Single Crystals

sample label	crystallographic orientation	$[UO_2^{2+}]_{initial}$ ($mol \cdot L^{-1}$)	pH
RCU2	(110)	10^{-2}	1.5
RCU4	(110)	10^{-4}	3.0
RCU7	(110)	10^{-7}	3.0

mixture was stirred for 12 h. Then, 40 μL of the uranyl stock solution was added to the suspension, to reach an initial concentration of metallic cation equal to 10^{-4} M, which was again stirred for 12 h. The suspension was then centrifuged at 3000 rpm for 30 min, and the equilibrium pH value was measured. To determine the final uranium concentration, 5 mL of the supernatant was removed and introduced in a borosilicate glass containing 1 mL of HNO_3 (0.6 M) solution. Then, 1.5 mL of a scintillation cocktail (Alphaex, Ametek) was added, and the mixture was stirred for 15 min to quantitatively extract the uranium from the aqueous solution. More details about this protocol can be found in the literature.[34] Finally, after centrifugation at 1900 rpm for 15 min, 1 mL of the organic phase was taken off for α-liquid scintillation counting. These measurements were carried out using a Tri-Carb 2700TR spectrometer (Packard). The sorption rate was calculated by comparing the initial uranium concentration to the final one in the supernatant. The uranium loaded powders were separated from the supernatant, washed, and stored in a drier, at room temperature, before spectroscopic measurements.

Taking into account the morphology differences between powder and single crystals, the above sorption protocol was slightly modified for the experiments involving the single crystals. The substrate was directly contacted with 1.5 mL of uranyl solution, in polypropylene tubes, without separation between hydration and sorption steps. After 24 h of gentle stirring, the single crystals were removed from the solution, washed with a small volume of acidified water (1 mL, pH = 3), dried, and stored at room temperature before further investigations. Three different initial uranyl concentrations were considered in order to investigate the effect of the surface coverage: 10^{-7}, 10^{-4}, and 10^{-2} M. Nevertheless, since uranium concentrations were as high as 10^{-2} M and in order to avoid uranium precipitation, only pH = 1.5 and pH = 3 were considered, which allowed one to keep only one uranyl species in solution whatever the concentration. Moreover, atomic force microscopy allowed one to check that there was no evidence for uranium precipitates even considering the higher uranyl concentrations. All the chemical conditions corresponding to the different samples discussed in this paper are reported in Table 1 for the powdered substrates and in Table 2 for the single crystals.

Spectroscopic Measurements. Spectrofluorimetry measurements were realized using a Continuum pulsed laser Nd:YAG (7 ns pulse duration), coupled with a tunable Panther OPO. Uranyl emission spectra as well as emission decays were collected at 77 K, on dried samples, with a Spectra-Pro-300 monochromator (Acton Research Corporation) equipped with a CCD camera (Princeton Instruments) controlled by a Princeton Instruments Inc. Model PG 200 pulse generator. The Princeton Instruments Inc. WINSPEC program was used to control this device. In order to get the best signal-to-noise ratio, the incident wavelength was monitored at 430 nm, and uranyl emission spectra were recorded in the range 450−600 nm. The uncertainties associated with the position of the emission band were 1 nm. Moreover, the fluorescence decays were fitted according to a multiexponential law using the IGORpro software. The variation of the calculated lifetimes obtained for several samples, prepared in equivalent conditions, was used to estimate the error bars associated to the decays. The accuracy was found to be better than 10%.

Results

Rutile powder was first characterized from a structural point of view. XRD measurements have shown that this solid was well crystallized (JCPDS file 21-1276). Moreover, no secondary phase has been detected. Since the total surface of the material in contact with the solution is a crucial point for sorption experiments, the specific surface area was determined (N_2-BET method) and found to be 4.9 m^2/g. In other respects, since it is well-established that the (110) crystallographic orientation is the main one for rutile powder,[35] then it is possible to estimate the surface coverage in the experimental conditions from crystallographic considerations and specific area value. The surface oxygen density is around 5 atoms/nm^2 for (110) face, which leads, for a mass-over-volume ratio equal to 20 g/L and $[U(VI)]_{ini} = 10^{-4}$ M, to a maximum surface coverage which cannot exceed 20% of a monolayer. Finally, for the U(VI)/crystal systems, an initial uranium concentration as low as 10^{-7} M was needed to study surface coverages comparable to the powder systems. For the higher uranium initial concentrations (10^{-4} and 10^{-2} M) used for the crystal samples, no evidence for U(VI) precipitation was found from AFM measurements, which is in agreement with our previously published results obtained using X-ray absorption spectroscopy.[36] Indeed, grazing EXAFS experiments had been carried out for both UO_2^{2+}/TiO_2 (110) and UO_2^{2+}/TiO_2 (001) systems with the same experimental conditions as in this paper, and any evidence for U−U contribution was detected, which led to conclude that there was no uranium precipitate or multilayer sorption on the titania surface.

In order to identify both sorption sites on the oxide and uranyl surface complexes, TRLFS spectroscopy was performed for both single crystals and powders. Preliminary experiments performed at 298 K using 390 nm as excitation wavelength have evidenced a blackening of the substrate which led to a total quenching of the uranyl fluorescence after a few minutes of irradiation. In order to avoid this problem, all the optical measurements were performed in liquid nitrogen (77 K), and the incident wavelength was monitored at 430 nm, which allowed one to obtain the best signal-to-noise ratio for the studied systems. Nevertheless,

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(35) Jones, P.; Hockey, J. A. *Trans. Faraday Soc.* **1971**, *67*, 2679.

(36) Den Auwer, C.; Drot, R.; Simoni, E.; Conradson, S. D.; Gailhanou, M.; Mustre de Leon, J. *New J. Chem.* **2003**, *27*, 648.

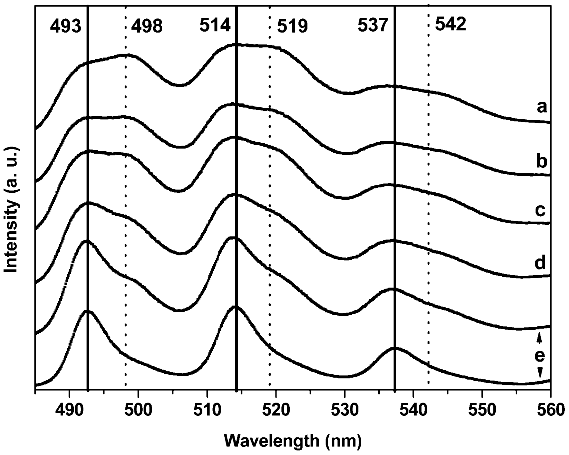

Figure 1. Uranyl emission spectra versus uranium initial concentration for rutile powder suspension: (a) RP90, (b) RP75, (c) RP50, (d) RP25, and (e) RP20.

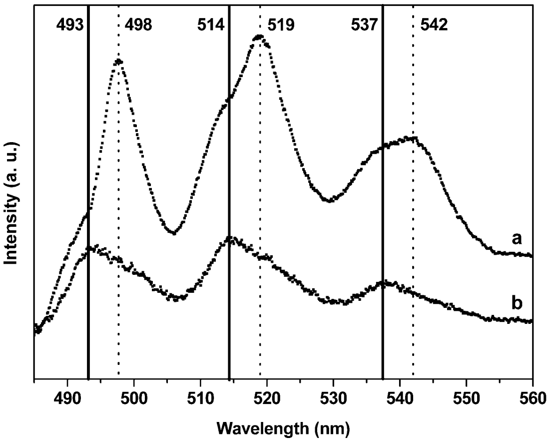

Figure 2. (110) single crystal—uranyl emission spectra versus uranium initial concentration: (a) RCU2 and (b) RCU4.

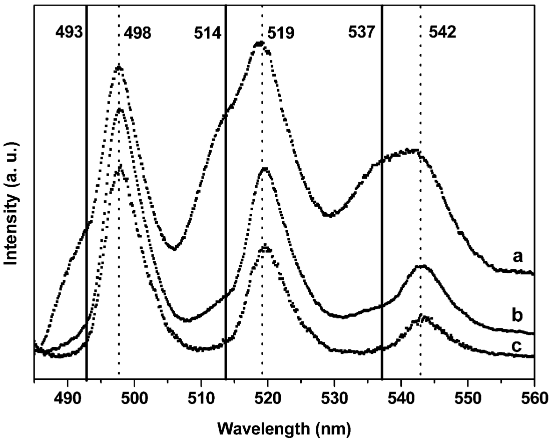

Figure 3. (110) single crystal—uranyl emission spectra versus time delay: (a) delay 0.1 μs, (b) delay 500 μs, and (c) delay 1000 μs.

it was checked that there was no change at all in the uranyl emission spectra between ambient temperature and 77 K.

1. Powder. The uranium retention by rutile surface was studied as a function of the pH of the suspension. As shown in Table 1, different samples corresponding to the whole sorption edge were analyzed (from 20 to 100% sorption rate).

As shown in Figure 1, the shape of the uranyl emission spectra is dramatically affected by the equilibrium pH value (i.e., the sorption rate). Two series of emission bands are clearly observed whatever the sample considered: 493/514/537 nm (named A) and 498/519/542 nm (named B), which account for the presence of two uranium environments on the surface. Moreover, since the positions of the emission bands are unchanged whatever the pH value (from 3 to 5), it means that the nature of the uranium surface complexes does not depend on the uranyl speciation. In other respects, the relative intensity of the second series (B) increases as the sorption rate increases. Indeed, while series B presents a low intensity for sample RP25 (relative to series A), the respective intensities of both series are quite similar for the highest sorption rate (sample RP90). Associated decay times were also recorded for all samples. Two lifetime values were necessary to properly fit the decay curves, whatever the equilibrium pH value: 55 and 185 μs, which is another evidence for the presence of two uranium surface complexes. Since the two lifetimes differ by a factor near 4, time-resolved experiments can be used to address one emission band series to one decay time. These experiments (not shown here) have evidenced that the shorter lifetime (55 μs) corresponds to series A and 185 μs is related to series B.

If, at this stage, it is clear that two uranium surface complexes are formed on rutile, no information is available about the actual nature of both species. Then, complementary studies are required, especially considering well-defined surfaces such as single crystals.

2. Rutile TiO_2 (110). Considering the same experimental approach, uranium loaded crystals were analyzed using TRLFS measurements. Investigations have been carried out on three (110) single crystals on which uranium ions have been sorbed at different initial concentrations (10^{-7}, 10^{-4}, and 10^{-2} M) in order to check the effect of surface coverage. Table 2 summarizes the experimental conditions corresponding to the preparation of each sample. Although the corresponding fluorescence spectrum of the sample RCU7 ([U(VI)] = 10^{-7} M) was rather weak (not shown here), its shape was quite identical to the other ones. Fluorescence spectra obtained for the samples labeled RCU2 and RCU4 (relative to U(VI) concentration of 10^{-2} and 10^{-4} M, respectively) are presented in Figure 2. Both spectra exhibit the same emission bands as the one observed for the powders, located at 493/514/537 nm (series A) and 498/519/542 nm (series B). Nevertheless, while series A is the most intense one for sample RCU4, series B becomes more intense than series A for sample RCU2. This observation suggests that the same surface species are formed for both experimental conditions and that only their respective proportions depend on the surface coverage. Measurements of the associated decay times led to determine two lifetime values for both samples: 55 and 185 μs. By acquiring the emission spectra for different delays after the laser pulse (Figure 3), it was possible to address series A to the shorter lifetime, while 185 μs corresponds to the second emission bands (series B). Once again, these results clearly evidence the presence of two uranium surface species.

Discussion

Since the exact structure of the sorbed uranium species depends on both nature of the reactive surface sites and metallic cation species in solution, the uranyl speciation was first established in the studied experimental conditions. Indeed, the main assumption to interpret the sorption mechanisms is that only the existing uranium species in solution are expected to lead to the formation of surface complexes. The speciation calculations were performed considering the equilibrium values reported in the literature.[37−39] In perchlorate medium, the U(VI) speciation is very simple since the free uranyl species is the only one in solution until the pH value reaches 3.5 and remains the main one until pH 5. For the highest pH values considered in this work, some hydroxylated species are formed in solution such as $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$. Nevertheless, whatever the equilibrium pH value, the spectroscopic characteristics of the sorbed uranium surface complexes are the same, which indicates that their nature does not depend on the pH value. Thus, since for pH = 3 (where only free uranyl ion exists in solution) the surface species are the same as for pH = 5 (free uranyl ion and hydroxylated species in solution), it is possible to unambiguously conclude that the two observed surface complexes involve the reaction of free uranyl ion (UO_2^{2+}) with two different surface sites. Then, to identify the nature of both reactive surface sites, it is necessary to compare the results obtained for rutile powder and single crystals, where the surface structure (i.e., composition) is well defined.

It is well-established that a solid (oxide for example) in an aqueous suspension develops a surface charge depending on the pH value. This charge arises from the dissociation of water molecules at the interface, so-called hydration of the solid, and leads to a uniformly hydroxylated surface. This phenomenon has been widely reported in the literature and, in particular, for TiO_2 rutile (110) crystallographic plane.[40−42] A representation of this hydrated surface is presented in Figure 4. Three kinds of surface oxygen atoms can be distinguished: 3-fold oxygen atoms, which are not reactive toward sorption of cations, 2-fold oxygen atoms (called bridging oxygen in the following text), and single-fold atoms (called top oxygen in the text). Moreover, EXAFS results have already been published about the U(VI)/TiO_2(110) face and U(VI)/rutile powder, considering similar experimental conditions to those reported in the present paper.[36] We have demonstrated that the uranyl ion is sorbed on two surface oxygen atoms to form a bidentate complex. In other respects, a short distance was found (2.31 Å for the (110) orientation and 2.33 Å for the powder) between uranium and surface oxygen atoms, which is typical for an inner-sphere complex. Taking into account these conclusions and the above remarks about the surface oxygen atoms present on the (110) rutile crystallographic plane, three kinds of surface sites could be expected: bridging−bridging site, top−top site, and a bridging−top one (Figure 4). Nevertheless, from the spectroscopic investigation performed on both powder and (110) rutile, it is clear that only two of these sites are reactive toward UO_2^{2+} ion.

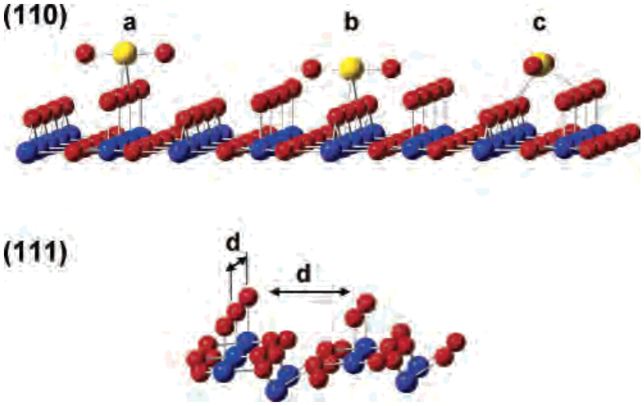

Figure 4. Schematic representation of the (110) and (111) crystallographic planes: oxygen atoms in red, titanium in blue, and uranium in yellow. (110) plane with the three possible surface complexes: top−top (a), bridging−bridging (b), and bridging−top (c). (111) plane: the distance between top oxygen atoms d is equal to 5.46 Å.

The study of the rutile (111) can bring further information to discriminate between the different surface sites expected. A schematic representation of the (111) face is proposed in Figure 4. For this crystallographic plane, the distance between two top oxygen atoms is 5.46 Å, which makes impossible the formation of an uranyl bidentate surface complex with U−O distances equal to 2.3 Å. Then, only the sorption of uranyl ion onto bridging−bridging and bridging−top oxygen atoms is expected, if it is assumed that the EXAFS results obtained for the (110) crystallographic orientation are still valid for the (111) one. TRLFS experiments were, thus, performed on the U(VI)/TiO_2(111) system. Although for this crystallographic face, the uranium fluorescence intensity is weaker than the one obtained for the (110) plane, the general behavior is similar. Two series of emission bands (series A and series B) were observed. They present the same lifetime values as for the (110) face and the powder: 55 and 185 μs. Nevertheless for the (111) face, no significant change was observed in the relative intensities of both emission series when the initial uranium concentration is increased. These results clearly indicate that the nature of the uranyl surface complexes is the same for (111) and (110) faces. Then, we can safely used the EXAFS results even if they were applied to the (110) crystallographic plane. Thus, the study of the (111) crystallographic plane allows one to conclude about the nature of the reactive sites toward free uranyl ion sorption onto TiO_2(110) and rutile powder: one surface site is composed of two bridging oxygen atoms, while a second one involves one bridging oxygen and one top oxygen atom.

The spectroscopic investigation performed on both powder and (110) single crystal has shown that one of these two

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(37) Grenthe, I.; Fuger, J.; Konings, J. M. *Chemical thermodynamics of uranium*; Elsevier Science Publishers: New York, 1992.

(38) Pashalidis, I.; Kim, J. I.; Ashida, T.; Grenthe, I. *Radiochim. Acta* **1995**, *68*, 99.

(39) Nguyen-Trung, C.; Palmer, D. A.; Begun, G. M.; Peiffert, C.; Mesmer, R. E. *J. Solution Chem.* **2000**, *29*, 101.

(40) Wang, L. Q.; Baer, D. R.; Engelhard, M. H.; Shultz, A. N. *Surf. Sci.* **1995**, *344*, 237.

(41) Bustillo, F. J.; Roman, E.; De Segovia, J. L. *Vacuum* **1989**, *39*, 659.

(42) Kurtz, R. L.; Stockbauer, R.; Madey, T. E.; Roman, E.; De Segovia, J. L. *Surf. Sci.* **1989**, *218*, 178.

sites seems to be more reactive than the second one for the lowest pH values. Then, the last point is to try to address the following question: which site could be the more reactive one. Some recently published results[43] obtained from surface second-harmonic generation (SSHG) study on the U(VI)/TiO_2(001) as a function of initial U(VI) concentration can be considered to answer this question. Indeed, the authors have shown that, in agreement with Grazing-XAS experiments,[36] it is possible to interpret the SSHG signal by considering two different sorption sites: the first one, which appears to be the more reactive one since it is observed for low U(VI) concentration (10^{-7} M), is composed by two bridging oxygen atoms, while the second one, less reactive, needs higher uranium concentrations to be formed and is composed of one top and one bridging oxygen atom. Then, some spectroscopic measurements, using TRLFS, were performed considering the U(VI)TiO_2(001) system. Once again, the spectroscopic characteristics of the uranium(VI) surface complexes were found to be identical to the ones observed for the (110) crystallographic face: (i) a first species characterized by emission bands located at 493/514/537 nm, an associated lifetime equal to 55 μs, and (ii) a second species characterized by 498/519/542 nm and 185 μs. Then, the U(VI) surface environment is identical for (001) and (110) crystallographic faces which justify the use of SSHG results obtained on (001) face to interpret the (110) results. Note that a similar conclusion has already been reported for cobalt interaction with titania. Indeed, cobalt sorption mechanisms have been studied for rutile (110) and (001) single crystals.[44] The authors have determined that the cobalt surface complexes are identical for both crystallographic planes. Moreover, since the formation of the second surface species (interpreted as a bridging−top complex) is favored by an increasing of the surface coverage, it can be addressed to a reaction between U(VI) and the less reactive site. Some recently published results obtained from quantum chemistry calculations (U(VI)/TiO_2(110) system) are in perfect agreement with the above experimental results and support our conclusion.[45] Indeed, it was demonstrated that the most stable surface complex corresponds to U(VI) sorbed onto two bridging surface oxygen atoms, while the U(VI) sorbed onto one bridging and one top oxygen atoms configuration is 5 kJ/mol less stable. Finally, the third structure (U(VI) sorbed on two top oxygen atoms) is nearly 10 kJ/mol less stable than the first one.

The comparison of the results obtained for different U(VI)/rutile systems allows one to conclude about the nature of the uranium surface complexes on the rutile powder as a function of the pH value. For pH corresponding to the bottom of the sorption edge, free uranyl ion mainly reacts with strong surface sites which involve two bridging oxygen atoms. Then, as the pH increases, another surface species is formed arising from the reaction between free uranyl ion and a weak surface site composed of one top and one bridging oxygen atom.

Conclusion

The aim of the study was to identify the surface complexes formed after sorption of U(VI) on titanium dioxide (rutile phase). This goal was successfully reached by using TRLFS, which has evidence for the presence of two uranium surface complexes for the powder system. Moreover, the (110) crystallographic orientation being the main one for rutile powders, the study of the U(VI)/(110) rutile single crystal was carried out. Based on the spectroscopic characteristics of the surface species, it was concluded that the nature of the uranium surface complexes was the same for (110), (111), and (001) crystallographic orientations and rutile powder. This result led to conclude about the nature of the two uranium surface complexes: the first one, which is the main one observed for the bottom of the sorption edge, arises from the sorption of free uranyl ion on two bridging oxygen atoms, while the second one, which is favored as the sorption rate increases, involves the reaction of free uranyl ion onto one bridging and one top oxygen atoms.

This structural study allowed one the definition of the sorption equilibria, by way of an experimental characterization of the sorbed species and reactive surface groups. These results are of primary importance since they reduce the number of assumptions and fitting parameters needed for the modeling of quantitative retention data obtained under the same experimental conditions. Thus, the calculated sorption equilibria constants appear to be more realistic since they can be determined without any assumption on the components involved in the sorption equilibria.

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(43) Dossot, M.; Cremel, S.; Vandenborre, J.; Grausem, J.; Humbert, B.; Drot, R.; Simoni, E. *Langmuir* **2006**, *22*, 140.

(44) Towle, S. N.; Brown, G. E.; Parks, G. A. *J. Colloid Interface Sci.* **1999**, *217*, 299.

(45) Perron, H.; Domain, C.; Roques, J.; Drot, R.; Simoni, E.; Catalette, H. *Inorg. Chem. Commun.* **2006**, *45*, 6568.