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Chemical Forms of Hydroxyls on/in Zirconia: An FT-IR Study

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Abstract

The hydroxyls groups of a heat-treated sample of zirconia powder (1170 K, 24 h in O_2/H_2O) were studied by FT-IR transmission spectroscopy and compared with those of 'as-received' and air annealed zirconia samples. The surface studies were driven 'in situ' in a cell allowing heat treatments under either dynamical vacuum (10^{-6} hPa) or controlled atmosphere, e.g. deuterium. The hydroxyls on the 'as-received' sample were quickly exchanged by OD when, after deuteriation of the sample heat treated in water atmosphere, hydroxyls are still visible. Twenty-five percent of them could not be exchanged even after a 4 h extension of the deuteriation process. As a counter-proof in the case of an air treated sample a complete deuteriation of the whole hydroxyls was observed. This difference clearly manifests that, in water annealed zirconia, H species have entered the bulk of the material where they are trapped. © 1998 Elsevier Science Limited. All rights reserved

Résumé

Les groupes hydroxyls formés sur une poudre de zircone traitée durant 24 heures dans un mélange O_2/H_2O à 1170K sont étudiés par spectrométrie FT-IR. Les résultats sont comparés à ceux observés sur la poudre initiale non traitée et traitée à l'air à cette température. Ces études de surface sont menées 'in situ' dans une cellule qui permet un traitement en température soit sous vide dynamique (10^{-6} hPa) soit en atmosphère contrôlée par exemple le deutérium. Dans nos conditions expérimentales, les hydroxyls de l'échantillon non traité sont très rapidement deutériés alors que 25% des hydroxyls de l'échantillon traité en présence de vapeur d'eau ne peuvent tre échangés, même après une longue exposition de quatre heures. Comme contre-épreuve, à la même température, tous les hydroxyls de l'échantillon traité à l'air, sont deutériés. Ces différences de comportement montrent bien que pour la zircone traitée dans l'eau, des espèces H ont pénétré dans le coeur du matériau où elles restent piégées.

1 Introduction

For many years, zirconia has been extensively studied by a large number of techniques, for its application as refractory material, but also as a catalyst, as well as the product of oxidation of zirconium alloys. These last materials are widely used in nuclear power reactors as fuel cladding. The problem of the role and the diffusion of hydrogen in zirconia arose some years ago, when the influence of water vapour on the evolution of microcrystalline zirconia was evidenced,[1] and at the same time, when the nuclear fuel suppliers had to deal with high hydrogen content in the metallic cladding tubes.[2,3]

Moreover the surface properties of ZrO_2 have been largely studied as to their capacities for being used as catalysts or catalyst supports.[4–8] It exhibits a characteristic behaviour in dehydration, hydrogenation and hydrogen exchange reactions.[9] The adsorption of molecule probes on the surface allowed to identify the surface species and to characterize this surface. It is known[10,11] that some water molecules and even the H_2 ones can be

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adsorbed on the surface inducing new OH ions, remaining on the surface or migrating in the lattice. T. Sato *et al.*[1] showed that the tetragonal to monoclinic transformation of Y-TZP was accelerated in presence of water molecules (compared to air or vacuum), and that this transformation is accompanied by microcracks formation. Thus, in the cladding tubes, the metastable tetragonal grains that are present in the oxide layer may transform spontaneously to the stable monoclinic form during the corrosion by primary water and the corrosion can be enhanced. The knowledge of the chemical forms of hydrogen atoms in the zirconia is thus of paramount importance.

The purpose of this study is to analyze the hydroxyls (–O–H) of zirconia by Fourier Transform Infrared (FT-IR) transmission spectrometry and to discuss the results concerning the chemical forms of hydrogen both on the surface and in the bulk of zirconia samples when heat-treated in a O_2/H_2O atmosphere.

2 Experimental

Non-stabilized zirconia powder was supplied by CRICERAM (now Cezus-Chimie, France) and was similar to that previously used in XRD[12] and Raman[13] studies. It was obtained by reacting hafnium-free zirconium tetrachloride with water vapour. The B.E.T. specific surface was $20\,m^2\,g^{-1}$, and the main impurities were Cl (1,9 %) and Hf (450 ppm). Three samples were investigated: as-received, air treated for 24 h at 1150 K, and heat treated for 24 h at 1180 K in a 30% O_2–70% H_2O mixture at atmospheric pressure, as described in.[13,14] The main characteristics of these three samples are reported in Table 1:

All FT-IR spectra were recorded with Nicolet 5DX spectrometer in the range 4000–600 cm^{-1}. The resolution was 4 cm^{-1}. The surface study required a cell for in-situ experiment allowing heat treatment up to 1000 K under either dynamical vacuum or controlled atmosphere. The pure initial powder was lightly pressed on an inert inox grid which promotes a good heat transfer and mechanically steadies the pellet. The pellet was then fastened into the cell. The spectra were recorded at different temperatures but only those obtained after cooling down to room temperature (RT) are given in order to compare them reliably.

The starting point was the activation process of the samples which consisted in heating the sample under dynamical vacuum (10^{-6} hPa), step by step, with a 100 K increment, up to 780 K, each step during 1 h. So the surface was cleaned (i.e. physisorbed or lightly chemisorbed ions or molecules were removed from the surface). Nevertheless the spectra are characterized, as usual in surface studies, by a very low IR transmittance mostly brought about by severe scattering losses at about 4000 cm^{-1} and the region below 1000 cm^{-1} is entirely obscure because of absorptions of lattice vibrations. Then, at 780 K, deuterium was admitted in the cell at a 100 hPa pressure, and left to exchange with hydrogen atoms. The surface species including hydrogen atoms were identified by means of the frequency shift of the FT-IR peaks induced by the deuteration which allowed us to follow this reaction. A rapid exchange, occuring within 10 min, indicates that the accessible hydrogen atoms are located at the surface of the exposed sample, while a delayed exchange, occuring after several hours, tends to indicate that deuteration is taking place through a diffusion process of hydrogen from the bulk to the surface of the sample.

3 Results

3.1 As received sample

The infrared absorption spectrum of this powder, dispersed in KBr pellet, (in the region 900–200 cm^{-1}) is given in Fig. 1(a). Few broad bands are visible, all due to vibrational modes (stretching or deformation) of ZrO_2.[15,16] The Raman spectrum was previously given;[13] it displayed a mainly tetragonal (about 85%) ZrO_2 structure and was in agreement with XRD measurements.

The IR spectra (in the region of interest for surface studies, i.e. 4000–1000 cm^{-1}) recorded during the activation, from room temperature up to 780 K, are given on Fig. 2. The bands observed at about 3500 cm^{-1} are assigned to the stretching modes of the OH bound hydroxyl groups. The large stretching vibrational band ν(OH) at 3450 cm^{-1} decreases with increasing temperature, it acts for the physisorbed molecular water. After a

Table 1. Characteristics of samples. Tetragonal volume fraction and crystallite mean size are determined by XRD measurements[14]

	Anneal temperature (K) and time (h)	*Anneal atmosphere*	*Specific surface (BET) (m^2g^{-1})*	*Tetragonal content (XRD)*	*Crystallite mean size (nm)*
As-received	—	—	20	81%	15
Air treated	1150 K 24 h^{-1}	Air	6·0	8%	27·5
Water treated	1180 K 24 h^{-1}	30% O_2/70% H_2O	4·2	0%	31

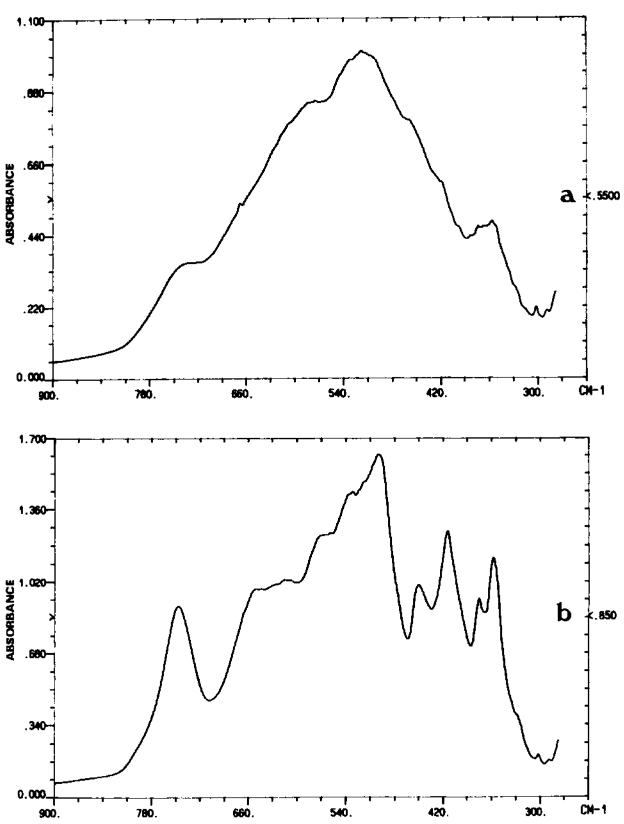


Fig. 1. FT-IR bulk-spectra (2 mg/400 mg of KBr) at RT temperature of the 'as-received' nonstabilized tetragonal zirconia (a) and of the steam-annealed monoclinic zirconia (24 h, 1180 K, 30% O_2/70% H_2O) (b). The spectrum of the air-treated zirconia (1150 K, 24 h) was similar to this monoclinic one.

780 K treatment, these remain only two bands at 3644 and 3450 cm^{-1}, due to OH groups chemically bound on the surface. In the same time, the spectrum below 1750 cm^{-1} was fastly modified by heat treatments. The bands at 1682 cm^{-1} (the bending vibration δ(OH) of H_2O), 1605, 1250, 1155 and 1025 cm^{-1} disappeared and two new bands at 1525 and 1460 cm^{-1} [Fig. 2(b)] appeared. Our results are summarized on the Fig. 2(f) with the difference spectrum displaying the disappearing/appearing species during in-situ activation.

The deuteriation allowed to fastly exchange the surface OH groups by OD ones as indicated by new bands at 2691 and 2569 cm^{-1} totally replacing the previous OH bands (Fig. 3). The ratios $\frac{3644}{2691}$ and $\frac{3450}{2569}$ are both equal to 1·35, in agreement with the harmonic oscillator approximation ($\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$) for the replacement of OH by OD (1·36). Because this change occurred within a few minutes, we conclude that the OH groups were actually on the surface. The other bands between 1400–1600 cm^{-1} were slightly shifted down (1507 and 1428 cm^{-1}) showing a light dependence of these carbonate bands to deuterium. These last bands could be assigned to monodentated carbonate forms because of a shift less than 100 cm^{-1} between the two values and moreover with a hydrogenated environment[17] perhaps CO_3H^- or a formiate ion. The presence of carbonates at the surface of zirconia are thought to be produced during the exposure to atmospheric CO_2.[6,18]

3.2 Air-treated sample

X-ray diffraction studies revealed that this sample was mainly monoclinic[14] with a few tetragonal grains remaining.

The FT–IR surface spectrum at RT [Fig. 4(a)] only displays a band at 3680 cm^{-1}. After activation at 780 K, an additional band appears at 3778 cm^{-1} [Fig. 4(b)]. Finally, after deuteriation, both bands shift within a few minutes to 2783 and 2710 cm^{-1} [Fig. 4(c)], whose frequencies are in very good accordance with the replacement of H atoms by D atoms. The very short time needed for this replacement indicates these groups are surface bands.

3.3 Water treated sample

The FT-IR spectrum, given on the Fig. 1(b), displays a lot of rather sharp peaks already studied.

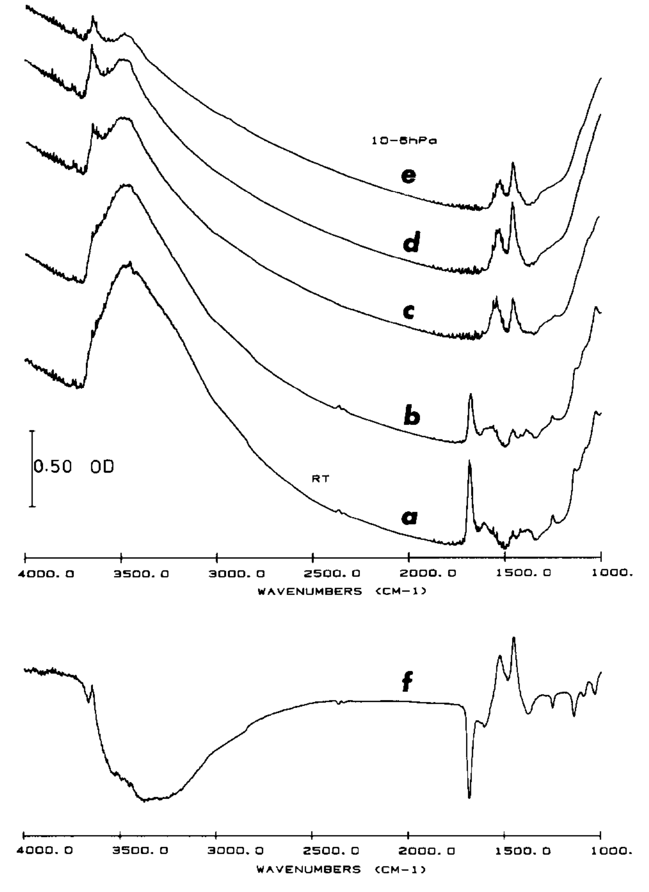


Fig. 2. Activation of 'as-received' t-zirconia. FT-IR 'in situ' absorption spectra of 'as-received' grid-supported pellet of zirconia powder: a: after evacuation at room temperature (RT); b, c, d, e: after in-situ treatment under dynamic vacuum at 480, 580, 680 and 780 K; f: difference spectrum between activation at 780 K and RT spectrum (e minus a). Bands downwards are due to disappearing species and positive bands to appearing species under activation. All spectra are given after cooling down to RT. Bands at ca 2300 cm^{-1} originate in variation of atmospheric CO_2 between reference and sample spectra.

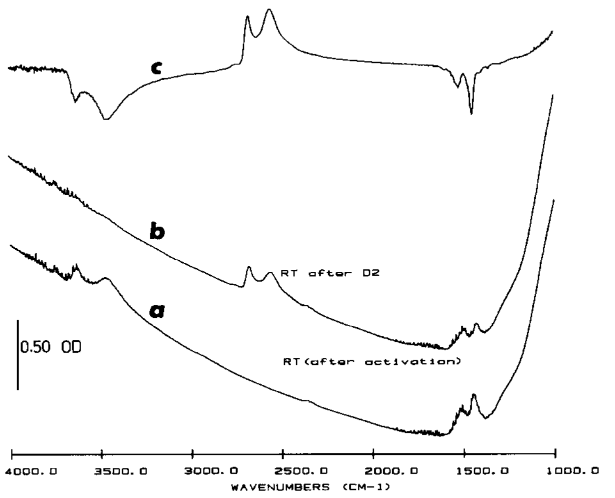


Fig. 3. Deuteriation of 'as-received' t-zirconia. FT-IR 'in-situ' absorption spectra of a grid-supported pellet, recorded at RT. a: after activation of 'as received' t-zirconia; b: after addition at 780 K of a 100 hPa dose of D_2 *for a few minutes*. The difference c = b−a features the modifications in the spectra of zirconia surface species after D_2 addition. Bands downwards are due to disappearing species.

The Raman spectrum of this sample[13] was typical of a monoclinic ZrO_2, as well as the XRD spectrum.

The activation up to 780 K leads to results quite different from the as received sample (Fig. 5):

- the broad band centered at 3450 cm^{-1} (physisorbed molecular water) weakens as soon as the sample is outgassed at room temperature and it disappears totally with increasing temperature;
- the narrow band at 3680 cm^{-1} is always observed but slightly decreases with temperature;
- at 370 K, a new band is observed at 3780 cm^{-1} which becomes, by heating up to 780 K, as intense as the band at 3680 cm^{-1}.

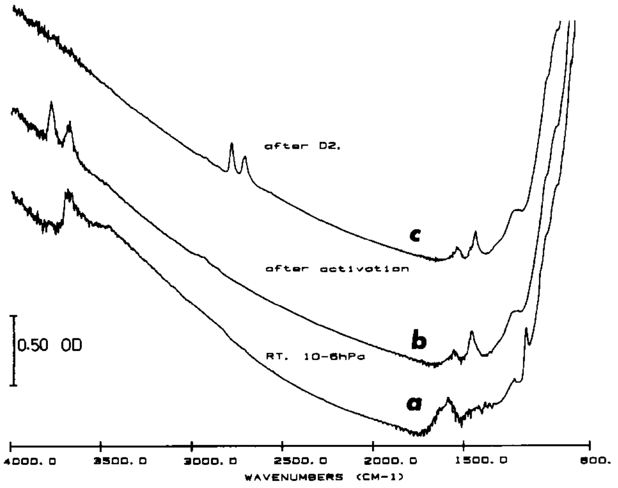


Fig. 4. Deuteriation of 'air-treated' m-zirconia. FT-IR 'in-situ' spectra, recorded at RT, of a grid-supported pellet annealed in air atmosphere: a: after activation of m-zirconia annealed in air atmosphere; b: after addition at 780 K of a 100 hPa dose of D_2 for a *few minutes*. The difference c = b−a features the modifications in the spectra of zirconia surface species after D_2 addition. Bands downwards are due to disappearing species.

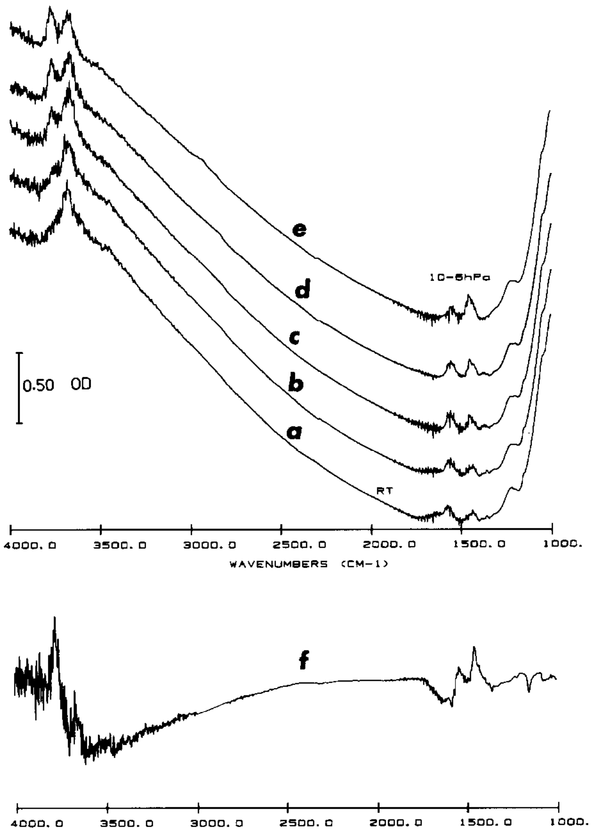


Fig. 5. Activation of 'steam-treated' m-zirconia. FT-IR 'in-situ' absorption spectra of a grid-supported pellet of monoclinic zirconia powder annealed in O_2/H_2O atmosphere: a: after evacuation at room temperature (RT); b, c, d, e, after in-situ treatment under dynamic vacuum at 380, 480, 580 and 780 K; f: difference spectrum between activated spectrum at 780 K and RT one (e minus a). Negative bands are due to disappearing species. All spectra are recorded at RT.

The difference spectrum, before and after activation at 780 K [Fig. 5(f)], displayed both an intensity increase of the 3780 cm^{-1} band and a small decrease of the 3680 cm^{-1} band. The observed absorptions at 1550 and 1450 cm^{-1} indicated that the surface is loaded with carbonates. The same results were found for the other air-heated sample.

The deuteriation at 780 K for four hours (Fig. 6) showed a shift of these bands at respectively 2713 and 2785 cm^{-1}. As seen above the ratios of the peak frequencies before and after deuteriation is equal to 1·36 and can be assigned to the replacement of OH by OD groups. However the deuteriation was not completely achieved. The slowness of this reaction indicates that these groups do not stand on the surface.

4 Discussion

4.1 Band assignments

The different stretching vibrations wavenumbers ν(O-H) on the tetragonal and monoclinic structures are given in Table 2 from the most reliable

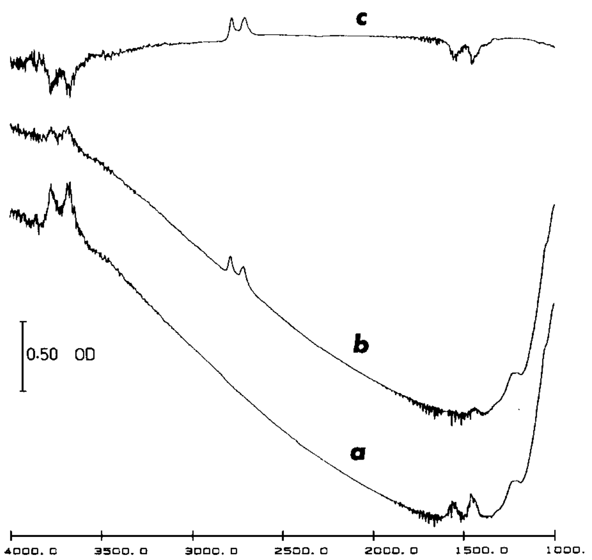


Fig. 6. Deuteriation of 'steam-treated' m-zirconia. FT-IR 'in-situ' spectra, recorded at RT, of a grid-supported pellet: a: after activation of m-zirconia annealed in O_2/H_2O atmosphere; b: after addition at 780 K of a 100 hPa dose of D_2 *for four hours*. The difference c = b−a features the modifications in the spectra of zirconia surface and bulky species after D_2 addition. Bands downwards are due to disappearing species.

Table 2. Literature data of stretching vibration wavenumbers of OH groups in zirconia.[11] Other authors[22–25] give values which can vary up to + 25 cm^{-1} according to the processing of samples, which is not always clearly explicited

		ZrO_2 *monoclinic*	ZrO_2 *tetragonal*
Zr-OH	OH_I	3760 cm^{-1}	3740 cm^{-1} 3720 cm^{-1}
Zr-OH-Zr	OH_{II}	3660 cm^{-1}	3660 cm^{-1} 3645 cm^{-1}
Bound water		3580 cm^{-1} 3480 cm^{-1}	3595 cm^{-1} 3440 cm^{-1}

literature data. Nevertheless we have to recall that other assignments have been proposed. The free OH band at ≅3660 cm^{-1} was indicative, according to Tsyganenko's classification[19] to tri-bridged OH groups on Zr^{4+}. Lately, in a high temperature study of hydrogen on m- and t-zirconia,[19] this assignment was taken again but not discussed. Moreover in this work the very intense band at 3744 cm^{-1} could arise from the SiO_2 stabilizer. Knözinger,[10] when discussing OH_I and OH_{II} groups brought more attention to O^{2-} co-ordination of the anion, OH_I being trigonally co-ordinated on $O_I{}^{2-}$ while the low frequency OH_{II} should be related to tetrahedrally co-ordinated $O_{II}{}^{2-}$. Notwithstanding this discussion, for the sake of convenience, we will refer hereafter to 'classical' OH_I and OH_{II}. These two representations characterized by rather narrow widths are assigned to free surface hydroxyls linked to one (I) or two (II) single cation Zr^{4+} and having different atomic environments respectively to the bridged and terminal groups.[21]

In Table 3, we have summarized the OH stretching vibrations bands observed in our experiments after cooling down to room temperature and the corresponding vibrating groups on/in the 'as-received', 'air-treated' and 'water treated' samples.

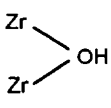
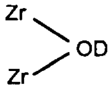
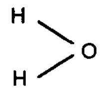
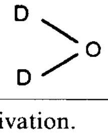
The bands we observed are in good agreement with literature data, so that their assignment is quite easy.

4.2 Influence of the heat-treatment

We must notice that the different behaviour of samples with temperature depends on previous treatments. Initially the as-received material is tetragonal while the material heat treated either in air or in O_2/H_2O is monoclinic. Activation at 780 K does not modify the phases (checked by Raman) and so the surface species on the samples are different: one kind of co-ordinated OH groups in the two latter cases and two kinds of co-ordinated OH groups in the former one, the stability of which being probably different. Besides, the deuteration evidences that a few OH groups are trapped in the lattice when the sample is O_2/H_2O treated.

The two kinds of bands at the surface of monoclinic zirconia did not appear at the same temperature. The thermal stabilities of the two species are different and the bridged $(Zr)_2OH$ (OH_{II}) was thought to be more stable because of the bidentate configuration.[21] Let us note that the behaviour of

Table 3. Summary of results and corresponding assignments. (s = strong, m = medium, w = weak, b = broad, f = fine)

Vibrating group		*As-received (t-zirconia)*	*Water treated (m-zirconia)*	*Air treated (m-zirconia)*
OH_I				
	Zr-OH	3780[a] m,f[b]	3778[a] m,f	
	Zr-OD	2785 m,f	2783 m,f	
OH_{II}				
		3644[a] m	3680[a,b] m,f	3675[a] m,f
		2691[c] m,f	2713[c] m,f	2710[c] m,f
Bound water		3450 s,b	3450 w,b	3455 w,b
		2569 s,b		

[a] After activation.
[b] Only partly accessible to deuteriation.
[c] After activation and deuteriation.

the two representations with molecule probes were also very different: for instance a small amount of $CHCl_3$ on ZrO_2 surface showed a marked decrease in the (OH_I) band and had only a little effect on the (OH_{II}) one.[21] The (OH_I) group at 3780 cm^{-1} was more reactive than the (OH_{II}) one at 3680 cm^{-1}.[8]

In the experiment involving the as-received material, only this more stable bridged form was observed on the surface of the zirconia grain. Morterra *et al.*,[7] characterizing three surfaces of microcrystalline stabilized tetragonal zirconia (t-ZrO_2) with several firing temperatures, concluded that the presence of a dominant band at 3660 cm^{-1} and the absence of a band at 3720 cm^{-1} were an indication of the (111) planes of t-ZrO_2, structured and/or reconstructed in the uppermost layer. Sometimes a band at 3760 cm^{-1} in t-ZrO_2 could be observed but its surprising sensitivity to heat treatment seems to indicate a lower surface stability.[7] Although a slight wavenumber shift occurs, we could propose that (111) planes are preferentially exposed on the surface of the tetragonal as-received powder.

When the sample was performed with the O_2/H_2O treatment, the OH_I band (3780 cm^{-1}) associated with the terminal form appears on evacuation above 370 K with a decrease of the (OH_{II}) band at 3680 cm^{-1}. The difference spectrum showed, in the same time, a decrease of the 3680 cm^{-1} band and an increase of the 3780 cm^{-1} band, which could suggest the transformation of a OH group bi- (or tri) co-ordinated to monocoordinated one.

By analogy with previous studies,[26–28] during O_2/H_2O treatment, the adsorption of water on the surface induced the migration of OH- ions from the surface of the grain into the lattice, resulting in nucleation defects and then promoting the tetragonal-to-monoclinic transformation. During activation process up to 780 K, these OH^- migrate faster than O^{2-} because OH^- has less charge and a size similar to O^{2-}.[26] According to Sato and Shimada[1] and Yoshimura *et al.*[26] who studied the Y-doped tetragonal ZrO_2, the formation of Zr-OH (Y-OH) at the surface of ZrO_2 seemed to be reasonable but their opinion was slightly different. While Sato and Shimada[1] imagined that the formation of OH^- caused the release of the strain which acted to stabilize the tetragonal phase, Yoshimura *et al.*[26] thought that the formation of ZrOH allowed the accumulation of stressed sites by migration of OH^- ions. Firstly, our result could be slightly different but our samples were not stabilized, contrary to other studies and perhaps the bridged form being the most stable is formed on the surface. The activation process was a reheating and so the OH^- ions, present in the lattice, could be removed to the surface to permit the Zr–OH species. Morterra *et al.*[7] had shown that by firing monoclinic zirconia at 1320 K, the intensity trend of the band at 3780 cm^{-1}, associated with monocoordinated OH groups, decreased also and only the OH_{II} form remained.

4.3 Influence of the deuteriation

After deuteriation of the as-received tetragonal sample, all the Zr–OH–Zr groups are moved into Zr–OD–Zr groups. When the sample is air-treated, deuteriation (Fig. 4) has every -OH groups shifted to -OD groups. In these two cases it means that all these species are easily accessible to deuteriation in our experimental conditions, i.e. all of them are on the surface of the powder. On the contrary, the -OH bonds observed in the O_2/H_2O treated sample were not all accessible: a few remained after deuteriation. They were trapped in the zirconia volume lattice (or in 'ink-bottles' if any). The chimisorption of water induced an OH^- migration from the surface to the bulk resulting in nucleation defects.[27] Some could remain inside the ZrO_2 lattice. A higher heating would have led to the migration of more OH^- groups to the surface because of an easier diffusion. About 25% of the initial OH groups were still visible on the spectrum (band at 3768 and 3668 cm^{-1}). This percentage was calculated from a repeated band-area calculation, assuming that this area is proportional to the number of vibrators and that all vibrators are identical. Only heat treatment in water atmosphere can induce such an OH migration inside the bulk.

In the literature,[1] it has been already shown that the tetragonal to monoclinic phase transformation in Y-stabilized tetragonal zirconia powder was easier by annealing in wet atmosphere than in dry atmosphere: the temperature was lower and the rate of the transformation was higher. The steam and particularly hydrogen seemed to play an important role as well in tetragonal to monoclinic transformation as for crystalline growth. The Raman spectra of as-received and heat-treated materials were in agreement with the above observations since the tetragonal to monoclinic transformation was performed by the heat treatment under wet atmosphere.

Besides, the surfaces of the most oxidic systems, exposed to the atmosphere, are covered quickly by a hydrated layer which is made up of hydroxyls groups belonging to the co-ordination sphere of surface cations and of undissociated water molecules co-ordinated to surface cations acting as Lewis acid centers.[6]

In oxide films formed on zirconium alloys, it has been show[2] that a lot of OH could be deuteriated. The width (600 cm^{-1}) (Fig. 8 in Ref. 2) and the wavenumber of the maximum absorption of the OH band clearly exhibit that these OH originate in physisorbed water H–O–H (for comparison see on Fig. 2(a) the absorbance of water, under vacuum) and could not originate in hydroxyls linked to zirconium; moreover, in order to observe the free hydroxyls, the bulk lattice vibrations intensity must be highly 'saturated', with absorbances superior to 6 OD, which is not the case in this experiment, and moreover the surface must be activated. Therefore, in this experiment,[2] the fact that the free hydroxyls were not put in evidence does not mean that they does not exist in 'massive oxide' because they represent only a minor part of all the OH groups of the film (see e.g. Figure 2). These authors[29] using the SIMS technique have made clear, from concentration profiles, that hydrogen and/or deuterium exist inside the oxide.

5 Conclusion

We analyzed the evolution, with activation and deuteriation, of the surface species on different zirconia. First we studied the carbonate species which are always present on the surface and could originate either in the manufacturing process or in the ageing of this reactive material at ambient temperature in atmospheric CO_2. To eliminate water adsorbed on the surface, the temperature must be raised up to about 580 K under vacuum in the case of monoclinic ZrO_2 and much higher for tetragonal one. Then we have shown that OH groups are physisorbed on the surface of 'as received' zirconia, in the form of Zr–OH–Zr bonds which were the most stable. By heat treatment in wet oxygen, hydroxyls penetrate into the zirconia volume and are displayed as Zr–OH groups. After such a treatment, both Zr–OH–Zr and Zr–OH are found on the surface of zirconia partly due to a migration of hydroxyl groups from the bulk to the surface but 25% of them still remain in the bulk. This is not observed when zirconia powder is only air-treated.

Further experiments are in progress with the aim to determine the activation energy of trapped OH and to study zirconia powders heat treated at 570/670 K under 10/15 MPa with respect to OH bondings on the surface and in the bulk. These physical conditions of temperature and pressure are of great interest in the nuclear industry.

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