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A Study of the Adsorption Sites on Thoria by Scanning Transmission Electron Microscopy and Fourier-transform Infrared Spectroscopy

Adsorption and Desorption of Water and Methanol

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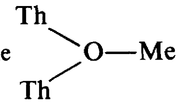
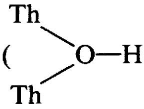
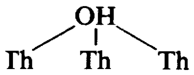
A study of the adsorption sites of thoria has been made using scanning transmission electronic microscopy (STEM) and Fourier-transform infrared spectroscopy (FTIR). The STEM study showed that the thoria surface was composed mainly of (110) (211) and (111) faces in about equal proportions. The infrared study of activated ThO_2 at 873 K indicated the existence of two remaining hydroxyl groups at 3660 and 3510 cm^{-1}. With water adsorption, a third one appeared at 3745 cm^{-1} which was thermally less stable. Methanol adsorption gave rise to three kinds of species: (i) one reversibly adsorbed at room temperature and linked by hydrogen bonds in which thoria acts as a proton receiver; (ii) two methoxy species characterized by ν(CO) bands at 1127 cm^{-1} (species I) and 1060 cm^{-1} (species II). Species I desorption bands led to methanol whilst species II, much more thermally stable, gave methanol, dimethyl ether and carbon monoxide. Species I, which corresponds to the hydroxyl species at 3745 cm^{-1}, are of the Th—OMe (Th—OH) type, and are formed on the (110) faces. Species II, which correspond to hydroxyl species at 3660 cm^{-1}, are of the  () type, and are formed on the (211) faces. The third hydroxyl species, characterized by the ν(OH) band at 3510 cm^{-1}, is probably due to species of the  type appearing on (111) faces. The stability and reactivity of the methoxy species are shown to depend on their structure, and therefore on the local arrangement of the surface.

It has long been recognized that the surface of a catalyst is not homogeneous, but is composed of various crystal planes and lattice imperfections. Structural differences between exposed crystalline faces involve different active centres, thus explaining that structure sensitivity occurs on oxide surfaces[1] as well as on metals.[2] The present work deals with the adsorption sites of thoria, an oxide active for alcohol synthesis[3] and which develops interesting properties in the process termed isosynthesis.[4]

Following our study of the acid–base properties of ThO_2[5] and the adsorption of H_2 and CO over ThO_2,[6] we report here results on the determination of the most frequently exposed planes of the microcrystallites of this oxide. Two techniques have been mainly used: scanning transmission electronic microscopy (STEM) and Fourier-transform infrared spectroscopy (FTIR). The first permits the determination of the relative importance of the different crystalline planes, while the second provides useful information on the nature of the adsorbed species: either hydroxyl groups (their wavenumber depending directly on their surroundings, as has been shown on alumina)[7], or species given by probe molecules. Among the various possible probes, water and methanol have been chosen, and a study of the adsorption of the former completes those for hydroxyl groups. For methanol, interesting results have already been obtained on various oxides,[8] the structural arrangement of the species formed depending on the local surface organization.[9]

Experimental

Materials

The ThO_2 (Rhône Poulenc) used had a specific area of 120 m^2 g^{-1}, a low pore volume (0.1 cm^3 g^{-1}) and a pore diameter of *ca.* 3.5 nm. It contained 0.7% N and 0.2% C, mostly as nitrates and carbonates. As it is a basic oxide,[5] these species are thermally stable.

Methods

STEM

A VG HB5 STEM equipped with a high-sensitivity TV camera to observe microdiffraction patterns[10] was used to study the local structure of the thoria. The surface giving rise to the diffraction pattern may be defined by the area scanned on the specimen, the limit being the size of the electron probe when stationary. The probe size and the angular size of the diffraction discs are determined by the beam convergence,[11] which in this case was typically 2 mrad, giving well separated discs whilst maintaining a high spatial resolution (of *ca.* 1 nm).

Diffraction patterns from individual grains attached to the carbon support film were obtained in the stationary-probe mode. These reveal the orientation of the grains with respect to the (flat) support. Our interpretation is based on the hypothesis that the grains, whatever their form, fall with their largest face parallel to the support film and thus perpendicular to the electron beam (this has been confirmed for alumina platelets in a similar study).[12]

Indexation of the diffraction patterns thus gives the orientation of preferentially exposed surface planes. Spherical particles would give rise to a random zone-axis distribution, weighted according to the number of symmetry equivalents.[13]

In attributing a surface plane to the corresponding zone axis we do not take into consideration the possibility of surface reconstruction. Weak-beam dark-field images show that the crystallites have smooth surfaces down to a scale of *ca.* 1 nm, but cannot give more precise details about the state of the surface.

FTIR

The infrared spectra were recorded at room temperature on a Nicolet MX-1 instrument (Caen) or a Digilab FTS-15E instrument (IFP). Self-supporting pressed discs (*ca.* 25 mg) were activated by heating under vacuum at 473 K for 12 h and then at 873 K for 4 h. After such a treatment only $\nu(OH)$ bands, due to residual hydroxyl groups, and weak bands at 1480 and 1330 cm^{-1}, due to residual carbonate and nitrate species, were apparent.

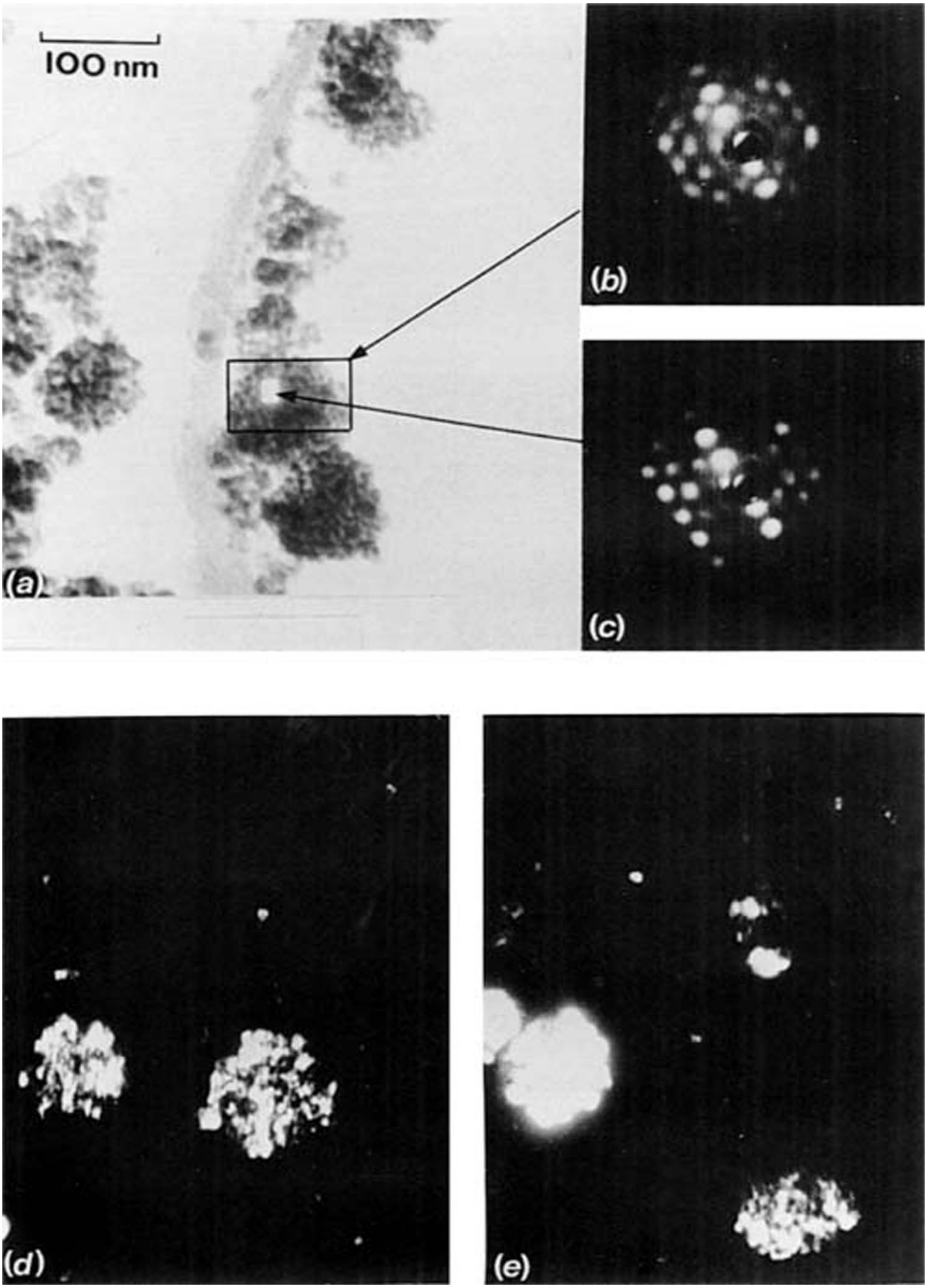


Plate 1. (*a*) Bright-field image of thoria. (*b*) Scanning microdiffraction pattern from boxed area of (*a*). The central dark disc is a hole in the observation screen to allow simultaneous imaging. (*c*) Spot microdiffraction pattern (the analysed area is shown by a bright-up marker). (*d*) and (*e*) Dark-field images, using two different diffraction discs, showing the size of coherent orientation domains.

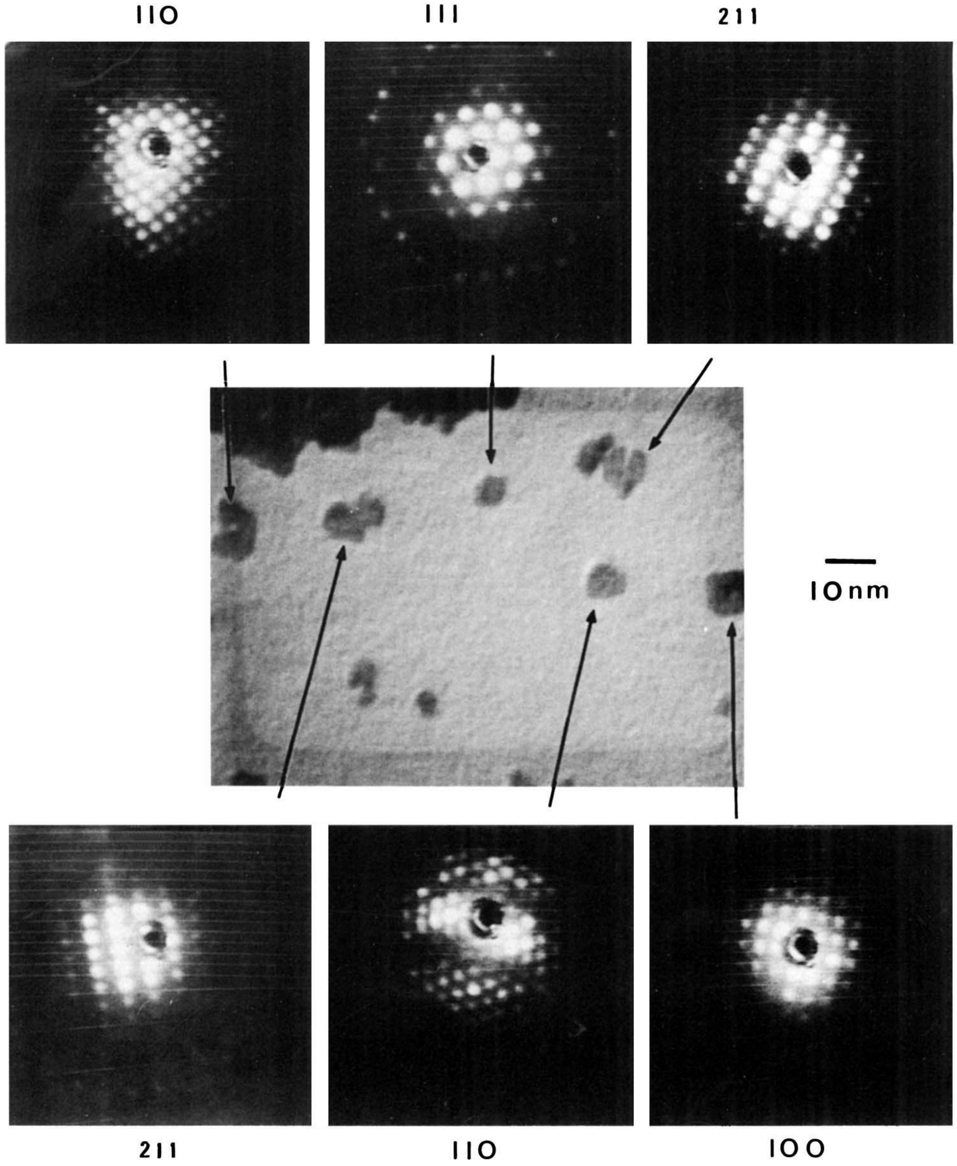


Plate 2. Indexed diffraction patterns from individual thoria crystals lying flat on the carbon support film.

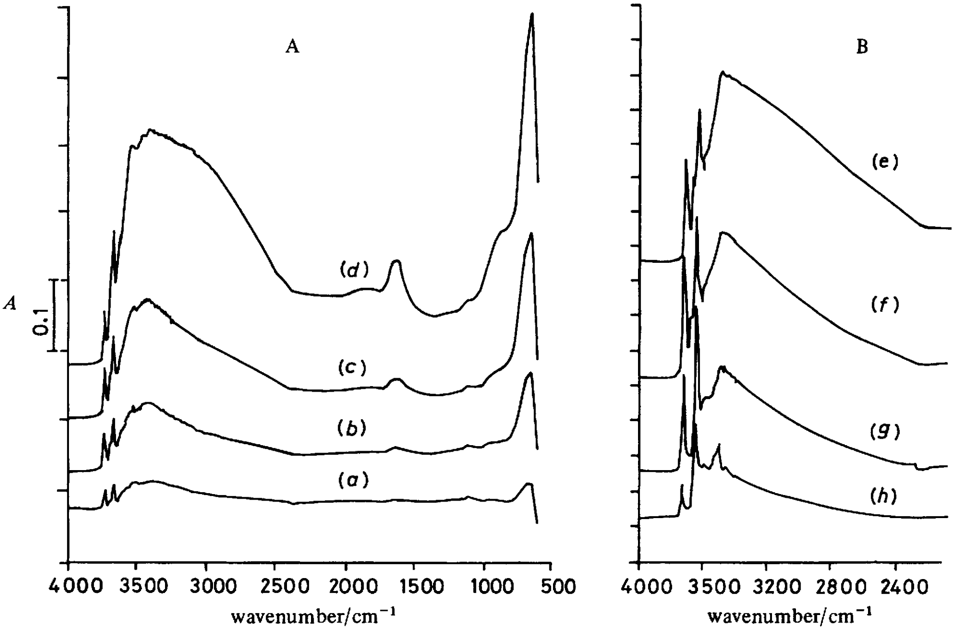


Fig. 1. (A) Infrared spectra of species given by water adsorption after addition of (*a*) 0.14, (*b*) 0.28, (*c*) 0.83 and (*d*) 1.5 molecule nm^{-2}. (B) Infrared spectra of species given by desorption after evacuation at (*e*) 293, (*f*) 373, (*g*) 473 and (*h*) 673 K.

T.P.D. of Methanol

On ThO$_2$ samples activated at 923 K under flowing helium, methanol was adsorbed at room temperature until saturation. Desorption was then carried out by heating at a rate of 5 K min^{-1} under flowing helium. The effluents were analysed by infrared spectroscopy using a gas cell, by mass spectrometry (Kratos MS 80 spectrometer) or by gas chromatography, using a 3 m column filled with a 50/50 mixture of chromosorb 103 and chromosorb 104 (Girdel N30 apparatus). Thermogravimetric experiments (with a Mettler MT 1 microbalance) were also carried out using the same process.

Results

STEM

The bright-field image of the specimen [plate 1 (*a*)] shows agglomerations of small grains of average individual diameter 10 nm. Electron diffraction of the agglomerates [plate 1 (*b*) and (*c*)] at different spatial resolutions shows them to be well organized, the grain orientation varying little (± 10° from the average) within a group. This is confirmed by dark-field imaging, in which grains with common directions appear together as bright regions [plate 1 (*d*) and (*e*) show dark-field images for two directions].

Diffraction patterns from individual grains could easily be obtained (plate 2), the thoria being well crystallized (no defect was detected either by diffraction or by high-resolution imaging) and constituting a strong scatterer. The observation of a large number of grains (more than fifty) showed roughly equal proportions of (110), (111) and (211) faces, these three accounting for 75% of the patterns recorded, with much lower proportions of (100) and (310) orientations; (123) and higher-index zone axes were very rarely seen.

FTIR

After the activation process, spectra show two ν(OH) bands at 3660 and 3510 cm^{-1}, with a weak shoulder at 3640 cm^{-1}.

Water Adsorption and Desorption

The adsorption of a small amount of water (0.12 molecule nm^{-2}) induces the appearance of two sharp bands at 3745 and 3670 cm^{-1} of equal intensity and another of low intensity at 3695 cm^{-1}. The spectrum [fig. 1 (A)] also presents a very broad band centred at *ca.* 3500 cm^{-1} and two others at 1635 (weak) and 670 cm^{-1}. Addition of supplementary doses of water increases the intensity of all these bands, except for that at 3695 cm^{-1}, which remains weak, while a new broad band appears at *ca.* 3000 cm^{-1}.

The intensity of the two bands at 3000 and 1635 cm^{-1} δ(HOH) greatly decreases by evacuation at room temperature, showing that they correspond to weakly adsorbed water. This water may be bound by a hydrogen bond to the hydroxyl groups giving rise to the two sharp bands at 3745 and 3670 cm^{-1}, since their intensity increases as water is evacuated.

Evacuation at increasing temperature (fig. 1 B) decreases the intensity of all the broad bands. At 373 K, the 3100 cm^{-1} band totally disappears while the 1635 and 3695 cm^{-1} ones are still detected. At 473 K, the molecularly adsorbed water is completely eliminated since the 1635 cm^{-1} band is not apparent. There remain only two sharp bands at 3745 and 3670 cm^{-1} and another at 3520 cm^{-1}, superimposed on the broad band centred at *ca.* 3500 cm^{-1}. The 670 cm^{-1} band is still very intense. At 673 K, the broad band at 3500 cm^{-1} disappears, bringing the 3525 cm^{-1} band into evidence. The sharp band at 3745 cm^{-1} is then much less intense. At 873 K, only the bands observed on the spectrum of the starting activated thoria are present.

The adsorption of D_2O leads to similar results [ν(OD) at 2760, 2706 and 2606 cm^{-1}; δ(DOD) at 1205 cm^{-1}]. The substitution of H by D does not produce any band equivalent to that of 670 cm^{-1} in the wavenumber range studied (4000–600 cm^{-1}).

These experiments have been completed by temperature-programmed desorption measurements. Activation of thoria by increasing the temperature shows that water desorption takes place discontinuously. An initial large desorption at 423 K is followed by a second at 650 K; a slow desorption is then noted at higher temperatures.

These results show the presence of at least three kinds of species. (i) Weakly adsorbed water, disappearing by evacuation up to 473 K and characterized by the 1635 cm^{-1} band. The sharp band at 3695 cm^{-1} is also due to this species and corresponds to the ν(OH) vibration of H_2O species with a free OH group. (ii) OH species bound by weak hydrogen bonds and characterized by the broad band at *ca.* 3500 cm^{-1}. They progressively desorb by increasing temperature up to 673 K. (iii) Free OH groups characterized by the sharp bands at 3745, 3670, 3640 (shoulder) and 3525 cm^{-1}. The band at the higher wavenumber is due to a relatively unstable free hydroxyl, as it is hardly detectable at 673 K. The 670 cm^{-1} band, still very intense after heating at 673 K, may be attributed to the δ(OH) vibration of hydroxyl groups responsible for the 3520 or 3670 cm^{-1} absorption.

Methanol Adsorption and Desorption

When 0.1 molecule nm^{-2} of MeOH is introduced, a very broad band between 3550 and 2440 cm^{-1} as well as bands at 2920 (sharp), 2900 (weak), 2865 (broad), 2800 (sharp and intense), 1445 (weak), 1127 (very sharp and intense), 1050 (broad), 1015 (very weak), 700 and 670 cm^{-1} (broad) are formed. By increasing the amount of adsorbed CH_3OH, an increase in the intensities of all bands is observed, except that of the 1050 cm^{-1} band which becomes a shoulder of a new band, broad and intense at 1060 cm^{-1} (fig. 2). Up to a value of 2.8 methanol molecule nm^{-2}, no gaseous phase is detectable in the cell.

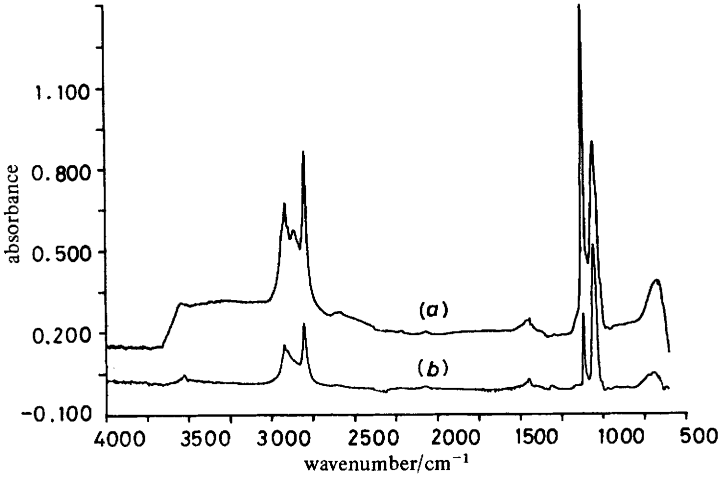


Fig. 2. Infrared spectra of species given by methanol adsorption on thoria (*a*) after addition of 3.2 molecule nm^{-2}; (*b*) after evacuation at 650 K.

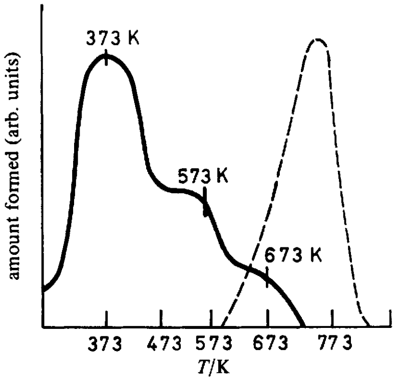


Fig. 3. Study by mass spectrometry of amounts of methanol (—) and dimethyl ether (---) formed at increasing temperatures from methoxy species on thoria.

Addition of further doses of CH_3OH increases a little more the intensity of all the bands and induces the appearance of others at 3550 (broad), 3100 and 2650 (very broad) and 1465 cm^{-1}. They can be assigned to reversibly adsorbed species.

The same results have been obtained when adsorbing MeOH on a ThO_2 pellet exchanged with $H_2{}^{18}O$ as in ref. (14) and then evacuated at 873 K.

Outgassing at increasing temperatures up to 673 K causes a decrease in the intensity of all bands between 3000 and 2800 cm^{-1} except that of the 2856 cm^{-1}, which vanishes totally. We also note a significant decrease in the intensity of the 1127 cm^{-1} band, whereas that of the 1060 cm^{-1} one is scarcely altered. The broad band between 3500 and 2400 cm^{-1} has completely disappeared. Between 473 and 573 K some very weak bands at 1565, 1375 and 1363 cm^{-1} appear temporarily, indicating the formation of a small amount of formate species.

These results allow us to conclude that at least three types of species are formed. One, characterized by a band at 1127 cm^{-1}, desorbs between 373 and 623 K (species I); the second, characterized by the 1060 cm^{-1} band, is stable at 673 K (species II). The third

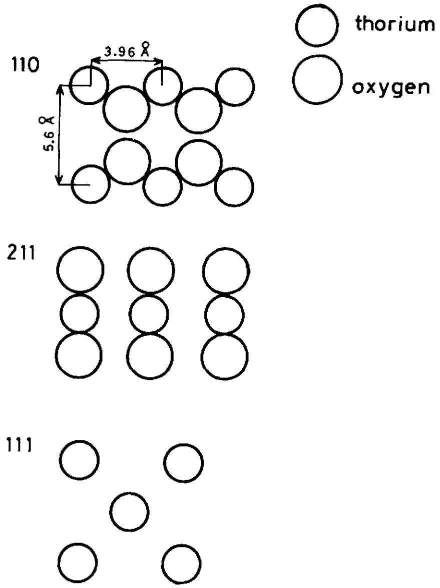


Fig. 4. Arrangement of the Th^{4+} and O^{2-} ions on the preferentially exposed faces of thoria.

is made up of the reversibly adsorbed species (species III). A fourth very similar to species II, may be distinguished from the latter as its characteristic band is at 1050 cm^{-1}. It only appears when the first dose of methanol is introduced (species II′).

The nature of the desorbed products has been studied by different methods: mass spectrometry, infrared spectroscopy and gas chromatography. They all clearly show (fig. 3) the occurrence of three desorption steps: (i) below 373 K there is a large methanol release, corresponding to species III, (ii) from 500 to 573 K another desorption of methanol takes place (species I); (iii) around 673 K a more complicated desorption process occurs (species II and II′), giving rise to the desorption of methanol, dimethyl ether and carbon monoxide.

Thermogravimetric measurements specify the amounts of the different species. The total amount of methanol adsorbed at room temperature is 4.2 molecule nm^{-2}, the irreversible quantity being 3.75 molecule nm^{-2}. From a plot of the weight variation *vs.* temperature, one can estimate the amount of species III (1.6 molecule nm^{-2}), species I (1.0 molecule nm^{-2}) and species II and II′ (1.15 molecule nm^{-2}).

Discussion

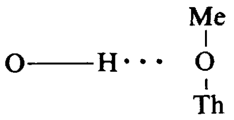
The thoria used in the present study has a surface area (120 m^2 g^{-1}) very similar to that prepared by Maj *et al.*[3] and claimed as one of the largest reported in the literature. X-Ray diffraction has confirmed that it is of the fluorite type, the thorium being positioned according to an f.c.c. lattice (cell parameter 0.56 nm).

The STEM study shows that the (110), (211) and (111) faces are the most frequently exposed. The (100), (310) and (123) are less exposed and will not be considered in the present discussion. The arrangement of the Th^{4+} and O^{2-} ions on the three preferentially exposed faces is shown in fig. 4.

The (110) face contains Th^{4+} ions with two anionic vacancies in the neighbourhood of the O^{2-} ions, which are coordinatively unsaturated (cus). The (211) face is formed by rows of cus Th^{4+} ions between two rows of cus O^{2-} ions. The (111) face only contains cus Th^{4+} ions, the oxygen ions, slightly below, being coordinatively saturated.

Let us now discuss the results obtained by infrared spectroscopy, beginning with those relevant to methanol adsorption. Species I and II (II′) resulting from methanol chemisorption on thoria are of the methoxy type: they are characterized by a $\nu_s(CH_3)$ vibration at 2805 cm^{-1}, *i.e.* at a low wavenumber, and a $\nu(CO)$ vibration (species I, 1127 cm^{-1}; species II, 1060 cm^{-1}; species II′, 1050 cm^{-1}) the wavenumber of which is higher than that observed with gaseous MeOH. Such features are typical of dissociative adsorption leading to methoxy groups.[15]

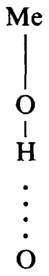
It is important to note that there corresponds to species I a broad $\nu(OH)$ band due to the dissociative adsorption. Its low wavenumber (between 3550 and 2400 cm^{-1}) favours the following type of structure:



$O\text{———}H\cdots\underset{\underset{\text{Th}}{|}}{\overset{\overset{\text{Me}}{|}}{O}}$

type I

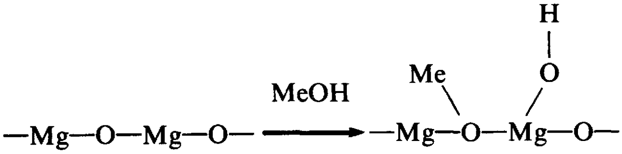
The reversible species (type III) is bound to the surface by a hydrogen bond. Considering the high basicity of thoria[5], the most likely species are:



type III

This would explain the high wavenumber of the $\delta(OH)$ vibration (1465 cm^{-1}) and the presence of the pair of broad bands at 3100 and 2650 cm^{-1} [$\nu(OH)$ in Fermi resonance with the first overtone $2\delta(OH)$].

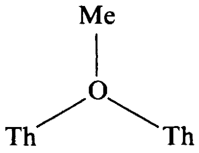
Our infrared results on thoria are similar to those observed by Tench *et al.*[16] on MgO. On such an oxide, the authors[16] considered that the most stable methoxy species are formed by the dissociation of the C—O bond:



In a later study, Tsyganenko *et al.*[8] mentioned this result and explained the difference between the methoxy species I and II by the coordination number (I or V) of the surface oxygens. Our result obtained from MeOH adsorption on ThO_2 exchanged with $H_2{}^{18}O$ does not support such a statement: considering that the surface oxygen has been exchanged with ^{18}O (as confirmed by the previous study on HCHO adsorption[14], we expect from the breaking of the C—O bond the formation of Me—^{18}O species characterized by a $\nu(CO)$ band[14] at 1086 cm^{-1} (type I) or 1017 cm^{-1} (type II). Since no band can be detected at such wavenumbers, we must conclude that type II methoxy species are formed in a similar way as type I, *i.e.* by dissociation of the O—H bond.

Dissociation of methanol needs pairs of sites formed by coordinatively unsaturated ions Th^{4+} and O^{2-}. Only the (110) and (211) faces of the three preferentially exposed faces present such pairs of sites. On the (110) face the orientation of the free valences of Th^{4+} ions and the position of the O^{2-} ions allow only the formation of MeO species bound to a single thorium ion. The released hydrogen adsorbed on an adjacent O^{2-} ion creates a hydroxyl group able to form a hydrogen bond typical of species I.

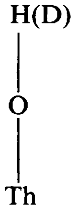
On the other hand, the orientation of the free valences of Th^{4+} ions on the (211) faces allows the formation of bridged methoxy groups:



species II

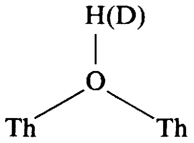
Such species would therefore result from the surface ion arrangement on the (211) face. Note that the number of species I and II obtained by thermogravimetric measurements is in agreement with the STEM results showing the almost equal abundance of faces (110) and (211).

The results obtained from water adsorption complete those relative to the residual hydroxyl groups on the activated samples and show the occurrence of a thermally unstable hydroxyl group at 3745 cm^{-1}. This corresponds to species I given by methanol and therefore can be assigned to the following Th—O—H group:



species I 3745 (2760) cm^{-1}

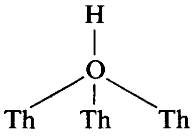
We assign to species II the hydroxyl group at 3670 cm^{-1}, which is much more stable:



species II 3670 (2706) cm^{-1}

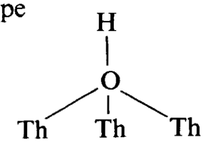
Such an assignment is in agreement with Knözinger's considerations on alumina:[7] the ν(OH) frequency of bridged hydroxyl groups is lower than that of monodentate ones.

The third OH group in the spectrum of ThO_2 has a very low wavenumber (3510 cm^{-1}). It may be considered as due to OH groups slightly perturbed by hydrogen bonding, as is the case for that on ZnO at 3444 cm^{-1}.[17] However, such an assignment can be discarded, since activation of thoria at high temperature does not perturb the 3510 cm^{-1} band. Another possibility is to consider that these hydroxyls are located in the bulk, as for silica.(18) They would then be unperturbed by surface adsorption processes and not exchangeable with D_2O. This is not in fact the case, leading us to propose a third possibility, that these hydroxyls would be arranged as follows:



which is quite possible on the (111) surface, one of the three preferentially exposed ones.

H_2O adsorption and desorption at 673 K leads to the 3745 and 3670 cm^{-1} bands and also a broad band near 3550 cm^{-1}. These certainly arise from water dissociation on Th—O couples such as those presented by the (110) or (211) faces. The OH^- formed is adsorbed on a Th^{4+}(cus) atom, leading to OH species I or II according to the type of face. The proton gives another OH group by adsorption on an adjacent O^{2-}(cus) surface atom. This latter group is of the type



explaining the appearance of the 3550 cm^{-1} band.

The fact that singly bonded or bridging methoxy and OH groups correspond to different frequencies accounts for results obtained in organometallic chemistry. For instance, the OH group of Me_3SiOH (an Si—O—H group like species I) corresponds to a band at 3737 cm^{-1} in the gas phase.[19] Its wavenumber is higher than those characteristic of species II {ν(OH) = 3643 cm^{-1} in the case of $[Me_2GaOH]_4$ in CCl_4 solution}[20] or of species III {(ν(OH) = 3595 cm^{-1} in the case of $[Me_3PtOH]_4$}.[21] Moreover, experiments in progress(22) show that the addition of water or ethanol to bridged methoxy species (species II) transforms them into species I, in agreement with the expected behaviour of bridged species according to ref. (23).

It is therefore possible to couple the results obtained by STEM and FTIR spectroscopy and to conclude that the local arrangement of ions on some faces induces the formation of different types of species. Their thermal stability depends on their structure, according to whether they are monodentate (methoxy groups of type I are easily desorbed as methanol) or bridged (desorption of methoxy species of type II leads to dimethyl ether and CO). Work is in progress to show that reactivity also depends on the structure of species formed, *i.e.* on the adsorption faces.

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