Infrared Surface Characterization of AIF₃

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Three specimens of crystalline AIF₃, coming from different preparation routes, have been examined: no major differences were found in the spectral region of the (v_3) fundamental mode, whereas the preparation process was observed to introduce appreciable differences in the background spectra that were ascribed to different bulk and surface impurities. Oxidic islands exist both in the bulk and at the surface of all preparations and when AIF₃ is derived from non-oxygen-containing precursors. In the latter case, species containing NH_x moieties exist, both in the bulk and at the surface. The surface hydrated layer of AIF₃ is made up of an extensive 'regular' component (*i.e.* a large amount of undissociated water molecules, coordinated to unsaturated surface AI^{VI} cations), and of an 'anomalous' component (*i.e.* some OH groups that are eliminated upon vacuum activation at relatively low temperatures). The adsorption of pyridine on samples activated by vacuum treatment at temperatures in the range 300–673 K indicates that on all specimens there are variable amounts of 'irregular' surface cations [*i.e.* coordinatively unsaturated surface AI ions with (quasi-)tetrahedral coordination], some of which are strong enough as Lewis-acidic centres to adsorb CO at ambient temperature. Coordinatively unsaturated surface AI ions with the 'regular' octahedral coordination are very weakly acidic, as revealed by the end-on adsorption of CO₂ at 300 K and by CO uptake at *ca.* 78 K.

The surface modification of catalytic transition aluminas, *i.e.* crystalline phases at Al_2O_3 with spinel structure, by the introduction of trace amounts of halide ions and, in particular, of fluoride ions has been carried out for a long time (*e.g.* see ref. 1 and 2). Surface fluorination is a suitable tool for modifying the acid-base properties of aluminas and their activity in various families of catalytic reactions.

Several experimental methods have been adopted to study the surface properties of fluorinated aluminas, and among them the IR spectroscopic approach has been used quite extensively.^{1,3,4} Data reported in the literature indicate that the surface chemistry of fluoride-modified aluminas can be explained simply by reference to the well known surface chemistry of the parent aluminas, even if the alumina (spinel) system has been modified by the presence in the surface layer of variable amounts of electronegative F^- ions, replacing OH and/or oxide ions. This seems to be basically true also in the cases in which extensive fluorination could be shown to bring about the segregation of a separate AlF₃ phase,³ so that the surface chemistry of the separate (low-surface-area) AlF₃ phase could not be revealed.

Recently, microcrystalline Al fluorides have also become increasingly important as catalysts *per se* and as supports for metal catalysts, as employed in various reactions such as the hydro-chloro-fluorination of light hydrocarbons. To the best of our knowledge, no systematic surface characterization of this type of adsorbent has been reported in the literature. This subject thus seemed to us to be of some importance. The present study should yield a preliminary understanding of the surface features of the support material whose structural and catalytic characterization is to be dealt with elsewhere.

AlF₃ exists in various crystallographic modifications,⁵ all of which have been adopted as catalysts and as supports for the preparation of metal catalysts. Moreover, various methods of preparation have been reported for AlF₃, which lead, following the experimental conditions, to the various crystalline phases with varying degrees of fluoride content. In view of this, the present contribution is devoted to examining the differences in surface properties among various polycrystalline AIF_3 systems, which belong either to different crystallographic phases or derive from different preparation routes.

Experimental

Materials

We investigated several polycrystalline AIF_3 systems that possess relatively high surface areas and are thus suitable for use as catalyst supports. Three preparations will be described here in some detail as they exhibit not only coinciding features but also some interesting differences in surface chemical behaviour.

Sample A

This was obtained by exhaustive fluorination with gaseous HF of γ -Al₂O₃ (ex pseudo-boehmite). It has a BET surface area of 29 m² g⁻¹. XRD data indicate that, in the bulk, it is a 74 : 26 mixture of γ -AlF₃ and δ -AlF₃ phases. This is an industrial product, termed MUC4 27/87, a proprietary catalyst of Ausimont S.p.A. Further preparative detail may be requested directly from the supplier through one of the authors (P.C.).

Sample B

This was obtained by the exhaustive fluorination of γ -Al₂O₃ with gaseous HF, using different fluorination parameters than those used in preparation A. It has a BET surface area of 25 m² g⁻¹. XRD data indicate that in the bulk it is a virtually pure β -AlF₃ phase.⁶ This is an industrial product, MUC4 90, a proprietary catalyst of Ausimont S.p.A. Further preparative detail may be requested from the supplier through one of the authors (P.C.).

Sample C

This was obtained by the thermal decomposition of $(NH_4)_3AIF_6$, carried out at 573 K in an inert atmosphere.

[High-purity $(NH_4)_3AIF_6$, was prepared by the addition of an aluminium bromide solution in absolute methanol to an excess of saturated methanol solution (*ca.* 0.5 mol dm⁻³) of ammonium fluoride.] Sample C has an Al content of 32.1% (the theoretical stoichiometric figure is 32.13%). The BET surface area is 24 m² g⁻¹. XRD data indicate that, in the bulk, it is a virtually pure γ -AIF₃ phase.

For all preparations, the F content was found to be in the range 64.5-66%, *i.e.* close to the theoretical stoichiometric figure (67.8%). All samples are referred to in the text and figures by the relevant symbol (A, B or C), followed by a numeral T_1 representing the temperature (K) at which the samples were activated *in vacuo* before the adsorption experiments and the recording of the IR spectra. Whenever a sample, vacuum activated at temperature T_1 , was rehydrated (at ambient temperature in the vacuum system saturated with water vapour), and was further vacuum activated at a temperature T_2 , this is represented by the symbol of the sample, followed by the symbols $T_1(r)T_2$.

Methods

Specimens of 'pure' AlF_3 were prepared for IR measurements either in the form of self-supporting pellets (*ca.* 10 mg cm⁻²) or, when optically thin samples were needed, in the form of thin-layer samples (*ca.* 3 mg cm⁻²), deposited from a suspension in isopropyl alcohol on a pure silicon platelet. To explore the low-frequency IR region (the spectral region of the fundamental vibrations of the solid), some samples were also prepared with the KBr pellet technique. The spectra of the latter samples were run in the air, whereas 'pure' AlF_3 samples were transferred after the preparation to the vacuum IR cell, where they underwent all thermal, adsorption and spectra collection treatments in a strictly *in situ* configuration.

Vacuum thermal treatments of all samples were usually carried out at $T \leq 650$ K, *i.e.* at temperatures at which the surface area and the crystalline phases are stable and which are as high as the temperatures normally employed in the catalysis by AlF₃-supported catalysts.

IR Spectra

IR spectra were recorded at a resolution of 4 cm^{-1} (spectra at 300 K) and 1 cm^{-1} (spectra at *ca*. 78 K) on Bruker FTIR spectrophotometers (113v and 48) equipped with both MCT and DTGS detectors. Owing to the *in situ* configuration adopted, the IR spectrum of the bare solid was used as a background in most of the adsorption experiments, so that subtractions of spectra and other manipulations could be performed routinely.

Results and Discussion

Background Spectrum

On passing from the isolated molecule (point group D_{3h}^{7}) to the crystalline state, AlF₃ becomes a virtually infinite threedimensional network of [AlF₆]³⁻ units, sharing corner fluoride ions (local point group O_{h}).⁸⁻¹⁰ The vibrational spectrum of anhydrous aluminium fluoride should thus be characterized by two fundamental modes (v_3 and v_4), corresponding to the stretching and deformation modes of the [AlF₆]³⁻ octahedra belonging to the symmetry species F_{1u} , allowed by the selection rules.^{10,11}

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The IR spectrum of anhydrous AlF₃ should not exhibit strong absorption bands at $\tilde{\nu} \ge 750 \text{ cm}^{-1}$,^{10,12} whereas in the case of hydrated forms of AlF₃ at least two additional (broad) bands should be localized in the spectral ranges around 3400 cm⁻¹ and 1650 cm⁻¹, due to the stretching and deformation modes of crystallization water.⁹

Fig. 1 shows the spectra of some of our AlF_3 specimens, run on samples of various forms, in order to cover all spectral ranges properly. The following features are apparent.

In the spectral region of the bulk fundamentals ($\tilde{v} < 800 \text{ cm}^{-1}$), the spectra of the three samples present only minor differences of resolution and relative intensity of the various components (for instance, the spectrum of preparation C is slightly better resolved), and this indicates that the crystalline phase and the preparation method have little effect on the sequence and orientation of the $[AIF_6]^{3-}$ octahedra. The v_3 mode, centred at *ca*. 670 cm⁻¹ (as reported by Shinn *et al.*,¹⁰) exhibits a weak low \tilde{v} shoulder at *ca*. 590 cm⁻¹ (reported in ref. 10 as typical of the γ -AIF₃ phase), and a broad high \tilde{v} shoulder at *ca*. 730 cm⁻¹ (not reported in ref. 10, and observed as an overlapping and unresolved component of the v_3 mode in ref. 12), which may be related to the first overtone of the v_4 fundamental.

In the spectral region above ca. 800 cm⁻¹, despite the structural order and crystalline purity of our AlF₃ preparations, the background IR spectra are more complex than expected in that they present some additional bands (ca. two orders of magnitude weaker than the fundamentals) and differ markedly from one preparation to another. In particular, the unexpected spectral features seem to depend mainly on the preparation route followed, rather than on the crystalline form of the resulting specimen. In fact: The background spectra of preparations A and B, though corresponding to different crystallographic phases, are fairly similar, and differ only in the intensity of the bands (much stronger on B than on A). The spectra of samples A and B are dominated by complex bands in the 3800-3500 cm⁻¹ and 1300-1000 cm⁻¹ regions, mainly ascribed to the stretching and deformation modes of 'structural' hydroxy groups, i.e. of OH groups which are mostly contained in the bulk of the solid, as is normally observed with aluminium hydroxides¹² and as reported by Bulgakov et al. for aluminium hydroxide fluorides.¹³ The bulk nature of most of these absorptions is demonstrated by their remaining virtually unperturbed throughout several vacuum activation and adsorption processes (e.g. compare curves A300 and A673 of Fig. 1(a); see also next section). Preparation C, though belonging to the crystallographic phase which is also the main component of preparation A, exhibits a very different background spectrum. In it, the spectral features ascribed for preparations A and B to 'structural' (bulk) OH groups are not absent, though they are only minor ones [e.g. compare the $\delta(OH)$ modes at ca. 1125 cm^{-1} on A673 and C623]: this is somewhat surprising, as preparation C derives from a non-oxygen-containing precursor, but it is not totally unexpected, as strong O 1s and Al 2p XPS peaks involving bound oxygen were observed by Scokart et al.³ on pure, low-surface-area AlF₃, coming from the thermal dehydration of $AlF_3 \cdot 3H_2O$. Other complex bands dominate the background spectrum of preparation C in the $3500-3000 \text{ cm}^{-1}$ and $1750-1250 \text{ cm}^{-1}$ regions. These bands are assigned to the stretching and deformation modes of several NH, groups that are derived from the incomplete removal of the decomposition products of $(NH_4)_3AlF_6$. $NH_2^$ groups (amido groups) are reported to absorb at 3350-3150 cm^{-1} [v(NH₂)] and 1550-1500 cm⁻¹ [δ (NH₂)] in amido complexes¹¹ and in surface NH_2 complexes,¹⁴ NH_3 has v_a and v_s stretching modes at 3400–3200 cm⁻¹ and the δ_a deformation mode at ca. 1640 cm^{-1} in both homogeneous and



Fig. 1 Transmittance IR background spectra in the 4000-450 cm⁻¹ range of some AlF₃ samples, thermally treated as shown by the sample symbols on the curves. K, KBr pellets, spectra run in air; P, self-supporting pellets, spectra run *in vacuo*; T, thin-layer deposits, spectra run *in vacuo*. (a) A and B samples; (b) C samples

surface complexes,^{11,14} and NH₄⁺ groups exhibit strong active modes (v_3 and v_4 , symmetry species F₂) at *ca.* 3150 and *ca.* 1400 cm⁻¹ in homogeneous compounds¹¹ and at *ca.* 3120 and *ca.* 1450 cm⁻¹ in surface species.¹⁴ The bands ascribed to NH₂⁻/NH₃ species (deformation modes at $\tilde{v} > 1500$ cm⁻¹) remain virtually unchanged throughout various activation and adsorption processes and are thus thought to be mainly due to decomposition products of the starting material, which remained trapped within the bulk of the newly formed solid. At $\tilde{v} < 1500 \text{ cm}^{-1}$ there are two strong complex bands that are ascribed to the v_4 mode of NH₄⁺ groups, and one of them (centred at lower wavenumbers and marked 1344 on the curve C623) is almost completely insensitive to vacuum thermal treatments, and is thus likely to be due to NH₄⁺-containing species trapped within the bulk of the solid. Still, the frequency 1344 cm⁻¹ is quite low for NH₄⁺ groups (even if trapped in closed cavities) and, as suggested by one of the referees and in view of the evidence for oxide impurities, the presence of trapped nitroderivatives (*e.g.* nitrito complexes and/or bridging nitro groups¹¹) could also be postulated.

Surface Components of the Background Spectra

In the case of oxidic microcrystalline systems, the surface unsaturation brought about by the termination of the crystallites is known to be saturated, upon exposure to the atmosphere, by the formation of a surface hydrated layer, made up of hydroxyls and of coordinated undissociated (*i.e.* molecularly adsorbed) water.

In the case of AlF_3 , in principle no coordinatively unsaturated (cus) oxide ions should be available at the surface, and one would thus expect the surface unsaturation of the crystallites to be compensated only by the coordinative adsorption of water molecules onto surface-exposed Al^{3+} ions which, owing to the crystal truncation, possess an incomplete octahedral coordination sphere. These coordinated water species are likely to be quite strongly held, owing to the presence of electronegative (charge-withdrawing) fluoride ions in the coordination sphere of the coordinating surface cus Al^{VI} ions.

The presence of coordinated molecular water at the surface of microcrystalline materials is usually made evident, in the IR spectrum, by the δ (HOH) mode centred at *ca.* 1630 cm^{-1.14} Fig. 1 shows that this is the case for samples A and B (see curves A300 and B300), as in these materials this spectral range of the background spectrum is free from other absorptions, whereas for samples C the observation of the δ (HOH) mode is not so straightforward.

Fig. 2(a) shows the differential absorbance spectra (*i.e.* absorbance spectra normalized against the spectrum of the solid, activated at 673 K) of the δ (HOH) mode of water coordinated at the surface of samples A (the behaviour of samples B is the same, and no spectra are reported). The partner stretching [v(OH)] modes of adsorbed water are (as usual) very strong, broad, and less clearly singled out in the high-wavenumbers range: they can be estimated to be at $\tilde{v} < 3400$ cm⁻¹ in Fig. 3(a) curves 1-4, and in the differential spectrum [2(i) - 3(i)].

The δ (HOH) spectra in Fig. 2(*a*) show that: the coordinated water species can be eliminated gradually from the surface of samples A upon vacuum activation at temperatures up to 623 K, thus confirming that the water molecules are coordinated quite strongly, *i.e.* more strongly than is normally observed on most metal oxides. Upon rehydration at ambient temperature, the adlayer of coordinated water molecules is restored virtually unchanged, if the first activation was carried out at $T \leq 573$ K (not shown in the figure). If the first activation was carried out at T = 623-700 K, the δ (HOH) band of the water adlayer formed upon rehydration is weaker [broken curve in Fig. 2(*a*)], even if the surface area of the adsorbent is unchanged. This is the first indication that the surface layer of microcrystalline AlF₃ undergoes irreversible modifications when treated *in vacuo* at relatively low



Fig. 2 Absorbance IR background spectra of AIF_3 , in the 1800–1500 cm⁻¹ range [(a) for samples A] and in the 1800–1200 cm⁻¹ range [(b) for samples C]. The samples were thermally treated *in situ* as indicated by the symbols on the curves. (---) Samples that were rehydrated and subsequently dehydrated at ambient temperature

temperatures. When the first activation is carried out at T > 700 K the surface area of the A and B preparations decrease and the δ (HOH) band at *ca.* 1630 cm⁻¹ forms, upon rehydration, with a much decreased intensity (not shown in the figure).

In the case of preparation C [Fig. 2(b)] note that: On these samples the observation of the $\delta(HOH)$ band at ca. 1630 cm^{-1} is made quite difficult by the presence, in the same spectral range, of strong background bands which are not eliminated but only partly modified upon vacuum activation, so that differential spectra cannot be used, and also regular absorbance spectra (i.e. spectra normalized against the spectrum of the source background) are much less 'clean' than in the case of samples A. In particular, a rather sharp band of medium intensity remains in the background at ca. 1640 cm⁻¹ after activation at any temperature, and is thus ascribed to the deformation mode of NH₃ (or H₂O) trapped in the bulk of the solid. Still, at least the overall behaviour of the water molecules coordinated at the surface of samples C can be observed, and is quite similar to that of samples A and B, confirming that the main composition, the stability and the incomplete reversibility of the surface hydrated layer of AlF₃ is the same for all preparations and all crystal phases examined.

It is peculiar to samples C that, when they are activated in a vacuum at up to *ca*. 670 K one of the two complex bands ascribed above to NH_4^+ ions, centred at *ca*. 1440 cm⁻¹, is progressively and irreversibly eliminated, whereas the other NH_4^+ band, also complex and centred at *ca*. 1350 cm⁻¹, remains virtually unchanged throughout all activation/ rehydration steps, as anticipated above. The band at *ca*. 1440 cm⁻¹ is ascribed to the v_4 mode of surface-exposed NH_4^+ ions^{11,14} and indicates that, in the γ -AlF₃ preparation obtained from (NH₄)₃AlF₆, part of the surface either con-

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Fig. 3 Transmittance IR spectra in the 4000–1800 cm⁻¹ range of samples A (a) and C (b), treated as shown by the symbols reported on the curves. (The numbers of the spectral sets were chosen so as to make the same treatment conditions of different samples correspond in the two sections.) (i) (solid line), spectrum run after the thermal treatment indicated by the sample symbol; (ii) (broken line), after the adsorption of ca. 6 Torr pyridine; (iii) (sample A513, crossed line), after pyridine evacuation at ambient temperature; (iv) (line with dots), as the corresponding curves (i), after D₂O adsorption and evacuation (exchange) at ambient temperature. Difference absorbance spectra are also shown.

tains adsorbed NH_4^+ ions which are desorbed at $T \le 670$ K, or is made up of an NH_4^+ -containing phase, which is irreversibly eliminated *in vacuo* at $T \le 670$ K. The partner band due to the IR-active v_3 mode of NH_4^+ , expected to absorb at *ca*. 3150 cm⁻¹, ^{11,14} is superimposed on (and thus cannot be distinguished from) the strong v(OH) modes of surface-coordinated water, the elimination of which is revealed in Fig. 3(b).

Fig. 3 reports the high-wavenumbers range of samples A (a) and samples C (b). This is the spectral range where, besides the elimination of surface water and of surface NH4 groups, dealt with above, the stretching modes of surface hydroxy groups might occur. Owing to the overwhelming intensity in this spectral range of several bands due to bulk species (which are not decreased by thermal treatment in vacuo), the isolation of the weak surface components in the spectra of Fig. 3 may be somewhat facilitated by the simultaneous presentation of some of the spectra modified by the adsorption at ambient temperature of pyridine (py): the spectral components perturbed by the uptake of a polar molecule such as py are ascribed to surface species. Moreover, some information on the presence and nature of spectral components due to surface OH groups may be derived from the exchange with D₂O and the possible creation of partner surface OD groups, shifted downwards in the spectrum by a factor of ca. 1.38.14 (In Fig. 3 the dotted traces represent the spectra obtained, with some AIF₃ samples, after exchange with D_2O and evacuation at ambient temperature.)

Fig. 3(a) shows that in samples A and B, which are derived from direct fluorination of alumina, a minor part of the hydrated surface layer is made up of OH groups, which are of more than one species. In fact: (i) adsorption of pyridine perturbs a weak and sharp OH band centred at *ca*. 3705 cm⁻¹, as well as a minor fraction of the strong and complex OH band at $\tilde{v} < 3700$ cm⁻¹, which turns out not to be due entirely to bulk hydroxy groups, but to contain also a broad component at *ca*. 3660 cm⁻¹ due to surface OH groups; (ii) exchange with D₂O [Fig. 3(a), curves 1(iv) and 2(iv), dotted lines] decreases the intensity of the OH bands at *ca*. 3705 cm⁻¹ and *ca*. 3660 cm⁻¹, while two weak 'free' OD bands are produced at *ca*. 2725 and *ca*. 2705 cm⁻¹, respectively.

The presence of surface OH groups on samples A (and B) indicates that the incomplete fluorination of aluminas left on the materials some oxidic 'islands', which are not only trapped in the bulk of the solid, but are also partly localized at the surface.

For the weak and well resolved surface OH species that absorb at ca. 3705 cm^{-1} , it can be observed that the band is quite sharp and centred at a fairly high frequency, and is thus due to OH groups that are free from H-bonding, also in the highest hydration stages [see curves 1-3 in Fig. 3(a)]. The band is quantitatively perturbed by the adsorption of pyridine and is not restored to any extent by evacuation at ambient temperature [see the enlarged segments (i)-(iii) of set 3, shown by the arrow in Fig. 3(a)]. The perturbation cannot be ascribed to a normal H-bonding interaction (usually reversible) of the OH species that absorb at ca. 3705 cm^{-1} with the N lone pair of pyridine, but must be ascribed to the side interaction of the OH species with a pyridine species adsorbed irreversibly (i.e. strongly chemisorbed) at nearby sites. The adsorption of pyridine will be dealt with in some detail in a later section, and this OH/pyridine interaction will be reconsidered. The band is labile: it is completely eliminated when the sample is evacuated at $T \leq 573$ K. In this respect, the behaviour of the band at ca. 3705 cm^{-1} is very different from that of all the 'free' OH species observed at the surface of transition aluminas,^{15,16} which require much higher activation temperatures to be eliminated. Upon

rehydration of the sample at ambient temperature, the band is restored virtually unchanged only if the first activation was carried out at T < 500 K (not shown in the figure). After activation at $T \ge 550$ K, the high v(OH) band is restored in part and with a modified profile [see curves 6 of Fig. 3(a)], whereas after activation at $T \ge 673$, the high \tilde{v} surface OH band is not restored at all, as shown by curves 7 of Fig. 3(a). This is a further indication that, at temperatures as low as 550-650 K, something is irreversibly modified in the surface layer of this AlF₃ preparation.

Fig. 3(b), relative to the high \tilde{v} spectral range of samples C, shows that the OH groups, whose stretching modes were observed to be just a minor component of the strong background spectrum in this range, have a surface component which is already perturbed by the adsorption of pyridine at the earliest stages of activation. Absorbance differential spectra (i.e. the spectral differences before and after pyridine uptake; e.g. the inset to curves 7) indicate that the surfaceexposed OH groups absorb at ca. 3695 and ca. 3675 cm^{-1} i.e. at frequencies fairly similar to those 'guessed' to be underneath the strong background OH contribution for samples A and B, whereas discrete OH components at $\tilde{\nu} > 3700 \text{ cm}^{-1}$ seem to be totally absent on this material. Exchange with D_2O at ambient temperature is extremely difficult on samples C, and after activation at ambient temperature or slightly above it [see the dotted traces (iv) of curves 1 and 2 in Fig. 3(b)] the exchange does not concern the 'free' surface OH groups, but only some coordinated water and, probably, some of the NH_x species, as demonstrated in curve 2 by the complex profile of the dotted-trace spectrum (iv) obtained after D_2O exchange. D_2O exchange demonstrates that some of the NH_x species are at the surface of samples C.

During the first dehydration run, the elimination (at $T \leq 673$ K) of the surface NH₄⁺ component discussed above modifies the surface layer so much that, after rehydration, the spectral profile in this range is completely different from the starting one [*e.g.* compare curves 2 and 7 of Fig. 3(b)].

After vacuum activation of the sample at 673 K (this stage is represented by the solid line spectrum of the curve set 5), rehydration with D_2O instead of H_2O produces the dotted trace (iv) of curves 5 (rehydration with H_2O produces the solid-line spectrum of the curve set 7): curve 5(iv) shows that the rehydrated samples C possess small amounts of several 'free' surface hydroxy species, whose frequencies are similar to those of the low \tilde{v} surface hydroxy species reported for samples A and B, but the high \tilde{v} hydroxy component (ca. 3705–2730 cm⁻¹ on samples A) is still totally absent even after the elimination of surface NH_x groupings.

Adsorption of CO at 300 K

CO is a weak Lewis base, and its adsorption on non-metal non-d systems at ambient temperature is known to reveal only small amounts of very strong Lewis-acidic centres. For instance, on Al oxidic systems CO is adsorbed at 300 K only on a few highly unsaturated surface Al ions that possess tetrahedral coordination (Al_{cus}^{IV}), yielding weak IR bands at 2190–2245 cm⁻¹.¹⁷ On surface-fluorinated alumina the CO band is reduced in intensity, owing to the elimination of some of the relevant sites, and its frequency increases, owing to inductive effects from adjoining electronegative fluoride ions.¹ Octahedrally coordinated surface Al centres (Al_{vus}^{VI}) are, on the contrary, too weak as Lewis-acidic centres to σ -coordinate CO at ambient temperature, so no CO uptake at 300 K is observed on α - Al_2O_3 ¹⁸ or on Al hydroxides.¹⁹

In all crystalline modifications of AIF₃ bulk Al ions occupy the octahedral cavities and, consequently, at the surface of AlF₃ 'regular' Al ions should possess only the octahedral coordination albeit incomplete due to crystal truncation. On the basis of the literature data quoted above, CO should not be adsorbed at 300 K on our AlF₃ preparations. Fig. 4 shows some data for the CO/AlF₃ interaction at 300 K, and shows that this expectation is only partly true, as CO bands do form, but are extremely weak. In particular, it can be observed that, as noted in the previous section for the bands in the background spectrum, the activity towards CO at 300 K depends much more on the preparation route than on the crystallographic phase. In fact CO bands of comparable intensity are formed on samples A and B (i.e. on different AlF₃ phases), whereas almost no activity towards CO is exhibited by samples C (i.e. on a phase coinciding with the main component of samples A, but obtained in a different way). No activity towards CO is developed in any of the samples after a vacuum activation at $T \leq 470$ K, *i.e.* in the temperature interval in which most of the abundant surfacecoordinated water is eliminated (see Fig. 2). This shows that the thermal desorption of the 'regular' hydrated surface layer, made up of water molecules coordinated to surface Al^{VI}_{cus} centres, does not produce Lewis-acidic sites that are capable of coordinating CO at ambient temperature, as expected. After vacuum activation of the sample at 510-600 K, an activity towards CO develops on AlF₃: it is almost negligible in the case of samples C (a tiny band forms at ca. 2215–2225 cm^{-1} , which remains almost unchanged upon activation at temperatures as high as 670 K), but it is appreciable in the case of samples A and B.



Fig. 4 Absorbance IR spectra of CO adsorbed at ambient temperature on AlF₃, preparation A (*a*), preparation B (*b*) and preparation C (*c*); [the spectra in (*c*) are reported with a four-fold ordinate scale magnification]. Samples were vacuum activated as indicated by the symbols noted on the curves. All spectra were run under $P_{\rm CO} = 120$ Torr, except for samples A513 and B573, for which three CO pressures were used ($P_{\rm CO} = 120$, 10 and 10^{-1} Torr)

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For preparation A two CO bands form that are well resolved (ca. 2190 and ca. 2220 cm⁻¹ on A513, and ca. 2195 and ca. 2230 cm⁻¹ on A573) and fully reversible (with slightly different rates) upon removal of CO from the cell, whereas in the case of samples B only the high $\tilde{v}(CO)$ component is observed. The latter band exhibits reversibility upon evacuation of CO from the cell, and a dependence of frequency and intensity on activation temperature very similar to those exhibited by the high \tilde{v} component of samples A. The spectral features of these CO bands are reminiscent of the features of the bands formed, upon adsorption of CO at ambient temperature on Al^{IV}_{cus} centres at the surface of transition aluminas activated at $T \ge 673$ K.^{1,17} The activity towards CO can be thus ascribed to cus (quasi-)-tetrahedral centres, created upon dehydroxylation of the oxidic islands, which were left in the surface layer by the incomplete fluorination. The oxidic islands are suggested by CO uptake at 300 K to be far more abundant on samples A and B than on samples C.

The high $\tilde{v}(CO)$ component of preparations A and B becomes broader and diminishes appreciably in intensity for samples activated at T > 600 K (e.g. compare A573/A673 and B573/B673). If the samples treated at T > 600 K are rehydrated all the activity towards CO is extinguished, as expected, and if they are further dehydrated at $T \ge 500$ K the CO bands form again, but the high \tilde{v} component no longer exhibits the profile and intensity it had on the original samples. Thus, at temperatures as low as 670 K, the vacuum activation begins to modify the surface layer of the AlF₃ systems (whose XRD and BET features are still unchanged) irreversibly, and the concentration of surface Al centres with a (quasi-)tetrahedral coordination that are active towards CO starts decreasing irreversibly. This is consistent with what is observed in the previous sections concerning the partly irreversible modifications of the surface revealed by the reconstruction, upon rehydration, of the hydrated surface layer. Needless to say, this behaviour on activation is quite different from the behaviour of transition aluminas, and it is therefore deduced that the oxidic islands at the surface of AlF₃ can be only vaguely assimilated to patches of non-fluorinated alumina.

Adsorption of CO at ca. 78 K

Some CO adsorption experiments have also been carried out at low temperature (nominally 78 K), to check if under these conditions Lewis-acidic activity could be exhibited also by the 'regular' Al_{vus}^{vu} centres. It is known that the acidic activity of octahedrally coordinated cus Al sites, which is indiscernible from CO adsorption measurements at ambient temperature, is also fairly weak at *ca*. 78 K.²⁰

Fig. 5(a) shows the spectral features of CO (40 Torr†) adsorbed at *ca*. 78 K on a sample of preparation A activated at various temperatures (note that the behaviour of samples B is the same and is not reported in the figure). On A300 (curve 1), the spectrum is dominated by a sharp band centred at 2165 cm⁻¹, with a broadish and weak shoulder on the low wavenumber side. On increasing the activation temperature (curves 2–4), the overall band of adsorbed CO shifts upwards (to *ca*. 2175 cm⁻¹), while it becomes less intense, much broader and distinctly asymmetric on the high-wavenumber side. These features are better illustrated in Fig. 6(*a*) which reports the spectral pattern relative to CO uptake and desorption on A300. For comparison, the figure also reports the CO bands observed for $P_{CO} = 10$ and 0.5 Torr, on A

^{† 1} Torr \approx (101 325/760) Pa.



Fig. 5 Absorbance IR spectra of CO adsorbed at ca. 78 K on AlF₃. The samples of preparation A (a) and preparation C (b) were treated in situ as shown by the symbols on the curves. Spectra in (a) were run under $P_{CO} = 40$ Torr. (b) Curves 1-4 relate to the adsorption of CO on C300, and curves 6-9 to the adsorption of CO on C573 ($P_{CO} = 2 \times 10^{-1}$, 1, 10 and 40 Torr). Curve 5 of (b) relates to the ca. 78 K adsorption of 40 Torr CO onto C623, rehydrated and subsequently evacuated at ambient temperature

samples activated at higher temperatures, where the band broadening and shift to higher wavenumbers with activation temperature are quite evident.

The spectral behaviour of CO adsorbed at *ca.* 78 K on A samples is complex, and suggests that two CO adspecies are formed and absorb in the 2160–2180 cm⁻¹ range. The first band is very strong and stands virtually alone in the case of A300; its maximum is centred around 2165–2170 cm⁻¹, its position being dependent on the CO coverage and activation temperature. This band diminishes in intensity for activation at higher temperatures. The second component, which is vir-



Fig. 6 (a) Absorbance IR spectra of CO adsorbed at ca. 78 K on AlF₃, sample A300, under decreasing CO pressures (in Torr) as indicated by the numbers on the curves. For $P_{CO} = 10$ and 0.5 Torr, the spectra of CO adsorbed onto samples A423 (broken line), A513 (line with dots), and A573 (crossed line) are also reported for comparison. (b) Absorbance IR spectra of the OH stretching region of sample A300, onto which CO is adsorbed and gradually desorbed at ca. 78 K, as shown in (a) of this figure. Some of the CO pressures (in Torr) are indicated on the curves

tually absent on A300 and is otherwise quite weak, becomes progressively resolved at $2170-2175 \text{ cm}^{-1}$ on samples activated at increasing temperatures. [Note that the poor separation of the two CO components is not due to lack of instrumental resolution, as the spectra at *ca*. 78 K were run at a resolution of 1 cm⁻¹, but is due to the fact that the two bands are separated by a spectral interval smaller than (or comparable to) the half-band width of either of the two bands].

On A573 [curve 4 of Fig. 5(*a*)], the second CO species centred at *ca*. 2175 cm⁻¹ is virtually the only one still present in the 2160–2180 cm⁻¹ range, while the weak band for CO adsorbed onto AI_{cus}^{IV} sites begins to appear at *ca*. 2230 cm⁻¹. Note that the last band is much weaker than either of the CO bands in the 2160–2180 cm⁻¹ range, confirming the low concentration and the defective nature of the relevant (quasi-)tetrahedral sites.

The two CO species in the 2160–2180 cm⁻¹ range can be assigned as follows. The species at lower \tilde{v} , which is dominant on samples activated at low temperatures (and thus still highly hydrated), is due to the H-bonding interaction of CO with surface hydroxy groups. This assignment is confirmed [Fig. 6(b)] by the specific and reversible perturbation produced, upon CO uptake on the 'free' surface OH component at *ca.* 3705 cm⁻¹ of sample A300, while a partner component is reversibly formed at *ca.* 3565 cm⁻¹. This band is redshifted, broader and much stronger than the parent band at *ca.* 3705 cm⁻¹, as expected of H-bonded OH groups.

The complex and broadish shoulder on the low \tilde{v} side of the CO band at 2165–2170 cm⁻¹ is most likely due to a weaker H-bonding interaction with other OH species, that cannot be seen in the presence of the strong bulk OH bands at 3680–3620 cm⁻¹ in the background spectrum. Nonetheless, minor reversible changes are observed, upon CO uptake, underneath the strong bulk OH bands [see the saddle marked 3653 in Fig. 6(b)].

The other CO species, which is located at higher \tilde{v} and is always quite weak, predominates on samples activated at higher temperatures (and thus less hydrated) and is thought to be due to the σ -coordination of CO onto weak surface Lewis-acidic sites. These may be represented by (part of) the Al^{VI}_{cus} centres produced by the vacuum thermal removal of surface coordinated water molecules, shown by the spectral pattern of Fig. 2(a). The CO band at ca. 2170–2175 cm⁻¹ is weak and reversible, typical of the weak CO/Al^{VI}_{cus} surface complexes already observed on other systems containing surface cus Al ions in octahedral coordination,^{19,20} but has v(CO) some 10 cm⁻¹ higher than in those cases. A higher stretching frequency implies a higher degree of σ charge release from the CO admolecules to the adsorbing centres, and is ascribed to the charge-withdrawing effect produced by the presence of electronegative fluoride ions in the coordination sphere of the adsorbing Al^{VI} ion.

The rehydration of A samples restores, to a variable extent, the starting activity towards CO. In particular, curve 5 of Fig. 5(a) shows that, if the rehydration is carried out on a sample first activated at $T \ge 570$ K, the band of H-bonded CO is formed with a lower overall intensity (indicating a lower concentration of the relevant OH groups), is more asymmetric on the high-wavenumber side (indicating a higher presence of the CO/Al^{VU}_{cus} σ -coordinated component) and exhibits a modified shoulder on the low-wavenumber side (indicating irreversible modification of the overall OH surface situation). Irreversible surface modification of samples A, brought about by activation at relatively low temperatures, was implied above by the background spectra and by the adsorption of CO at 300 K.

Fig. 5(b) shows spectra for the 78 K interaction of CO with samples C. The CO adsorption/desorption pattern relative to C300 [curves 1-4 of Fig. 5(b)] indicates that, besides a weak CO band at ca. 2165 cm⁻¹ relative to the H-bonding interaction with the scarce surface hydroxyls, another broad and complex CO band forms at 2155-2145 cm⁻¹. These frequencies, being only 2-12 cm⁻¹ higher than the frequency of gaseous CO, imply a weaker CO/support interaction. The virtual absence of the latter broad and low \tilde{v} component on C samples activated at $T \ge 570$ K [curves 6-9 of Fig. 5(b)] and on rehydrated C samples first activated at $T \ge$ 570 K [see the broken curve 5 in Fig. 5(b)] indicates that the relevant CO interaction does not occur at Lewis centres or on surface OH groups. It is most likely an interaction of the H-bonding type with some of the surface NH_x groups, which were shown in a previous section to be irreversibly eliminated from C samples upon vacuum activation at $T \ge 500$ K.

As for the high $\tilde{v}(CO)$ component (ca. 2170–2175 cm⁻¹), which develops after activation at $T \ge 500$ K and was ascribed to the formation of some CO/Al^{VI}_{cus} surface complexes, the CO adsorption pattern relative to C573 [curves 6–9 of Fig. 5(b)] indicates even more clearly than on samples A that the CO band of AlF₃ specimens activated at $T \ge 570$ K is double, with a component centred at ca. 2175 cm⁻¹ which forms first on adsorption and is more resistant to evacuation. The absence of the high $\tilde{v}(CO)$ component on rehydrated C samples [see trace 5 in Fig. 5(b)] confirms that this component ought to be ascribed to a weak interaction of the Lewis acid–base type (*i.e.* to CO/Al^{VI}_{cus} complexes, as postulated in the case of samples A and B).

Adsorption of CO₂

Carbon dioxide is widely used as a probe molecule in surface chemistry; its adsorption at ambient temperature is useful for revealing basic centres (i.e. 'basic' OH groups, and cus surface oxide ions, on which CO_2 yields various types of surface carbonate-like complexes²¹) and Lewis-acidic centres [*i.e.* cus surface cationic centres, on which CO_2 yields surface linear (end-on) complexes]. The last adspecies have been recently shown to be particularly useful in revealing weakly acidic centres as, for instance, in the case of AI_{cus}^{V1} sites at the surface of Al hydroxides.^{19,22}

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The interaction at ambient temperature of CO₂ with our preparations of AlF₃ indicated that no carbonate-like species form on any of the preparations investigated in any activation stage. This means that, even if oxidic islands and/or hydroxy groups remain in variable amounts at the surface of all of the AlF₃ preparations examined, their chemical features are such as not to reproduce nor simulate the adsorption behaviour of transition²³ and non-transition aluminas^{19,24} as far as the activity of basic surface centres is concerned. Also aluminas that are partly fluorinated in the surface layer were reported by Peri¹ not to form carbonate-like species upon CO₂ uptake. In this respect we think that the use of CO₂ adsorption/desorption as a tool to dose the surface basicity of fluoride-modified aluminas, as proposed recently,² is questionable.

Several end-on CO₂ complexes form, the variety and relative amounts of which depend more on the preparation route than on the crystalline phase. Some data relative to the formation of end-on CO₂ complexes at the surface of our specimens are reported in Fig. 7, where it can be observed that on all preparations a mild vacuum activation at up to 423 K (which was shown to correspond to the elimination of a large fraction of the undissociated coordinated water) brings about the formation of a sharp and symmetrical CO_2 band at ca. 2348 cm⁻¹ [mode Σ_{u}^{+}], which can be ascribed to the end-on coordination onto (some) Al_{cus}^{VI} centres. Note that this band is ca. 5 cm⁻¹ higher than in the case of Al_{cus}^{VI} centres at the surface of Al oxidic systems,^{19,23} most probably due to inductive effects from the nearby fluoride ions. After activation at temperatures up to 600 K, the CO_2 band due to Al_{cus}^{VI} centres becomes more complex (it becomes broader and asymmetric, and at least two components are partly resolved in the case of samples A573 and B623), while other CO₂ end-on complexes form at $\tilde{v} > 2360 \text{ cm}^{-1}$. The latter species, ascribed to the interaction with Al^{IV}_{cus} surface centres, predominate on samples A and B (especially on samples B), whereas on samples C the bands at $\tilde{\nu} > 2360 \text{ cm}^{-1}$ remain quite small, consistent with the scarce presence at the surface of this preparation of strong Lewis-acidic sites with a cus (quasi-)tetrahedral coordination, as postulated above.

The stronger nature of the CO_2/Al_{cus}^{IV} complexes is monitored by the higher spectral position (implying a higher degree of σ -charge release to the adsorbing sites), and by the much slower desorbability at ambient temperature, as reported previously²² and shown by the desorption patterns of A573, A623 and B623 (Fig. 7).

After activation at $T \ge 623$ K, the bands of CO_2/AI_{cus}^V complexes formed on samples A and B are modified [*e.g.* compare the spectra of samples A623 and A573 in Fig. 7(*a*)]. The component absorbing at the highest \tilde{v} (*ca.* 2380 cm⁻¹) diminishes in intensity, confirming once more the hypothesis that on these samples irreversible modifications occur in the surface layer even at relatively low temperatures, when no change in crystalline phase and/or of surface area occurs. Also, the behaviour of the oxidic islands at the surface of AlF₃ turns out to be different from that of transition aluminas.

After rehydration, and a further dehydration of the sample at 300 K, the band of CO_2/AI_{cus}^{v1} complexes is stronger than on the starting material. This is true for all AlF₃ preparations but is particularly evident in the case of samples C. It implies a possible incomplete rehydration (as already noted with coordinated water in Fig. 2) and, in the case of samples C (where the elimination of surface species containing NH₄⁺ and other NH_x functionalities has occurred), the creation of a 'cleaner' surface.

The severe surface modification of samples C, when treated at T > 600 K, is also confirmed in Fig. 7(c) by the spectrum



Fig. 7 Absorbance IR spectra obtained by the end-on adsorption of CO_2 onto various samples of AlF₃, preparation A (a), B (b) and C (c), treated *in situ* as shown by the symbols on the curves. All spectra refer to the adsorption under a CO_2 pressure of 10 Torr, but for three samples (A573, A623 and B623) for which few desorption steps are also shown. CO_2 pressures (Torr) were, from top to bottom, 10, 3 and 0.5 Torr for A573 and A623, and 10, 5, 1 and 0.3 Torr for B623

Adsorption of Pyridine

Pyridine is a strong base, and its adsorption is used very frequently in surface chemistry, both to distinguish Brønsted and Lewis acidity,²⁵ and to single out Lewis-acidic centres of different strength. Some data on the adsorption of pyridine on aluminium fluoride and hydroxyfluorides were reported, some years ago, by Bulgakov *et al.*²⁶⁻²⁸

Fig. 8 shows for some samples A in various activation stages, the absorbance spectrum in the 1800-1400 cm⁻¹ region run before and after pyridine adsorption/evacuation at ambient temperature. Note that the spectrum of adsorbed pyridine is complex and contains several different adspecies, which are described below in some more detail (Fig. 9). The overall intensity of the spectrum of pyridine adsorbed on A300 (i.e. the adsorbing capacity of A300 towards pyridine) is relatively small compared to the intensity of the broad band at ca. 1630 cm^{-1} that is due to coordinated water. Moreover, the pyridine uptake attained at ambient temperature involves sites different from those which coordinate water, as pyridine adsorption occurs without any appreciable ligand displacement of adsorbed coordinated water. (This phenomenon is common on some oxidic systems, e.g. TiO_2 ,²⁹ in which water coordination and pyridine chemisorption compete for the same sites.)

The vacuum thermal elimination of coordinated water, which occurs in the 300-630 K interval and has been



Fig. 8 Absorbance spectra obtained in the mid-IR range by the ambient temperature adsorption/desorption of pyridine onto AlF_3 , preparation A, activated at the temperatures (in K) indicated on the curves. Sets I (A300) and II (A423): (i) background spectrum; (ii) after admitting *ca.* 8 Torr pyridine; (iii) after pyridine evacuation at ambient temperature. Set III: (i) spectrum run after pyridine adsorption/evacuation at ambient temperature on A573; (ii) spectrum run after vapour adsorption/evacuation at ambient temperature on the sample of curve (i); (iii) sample (ii) after a further pyridine adsorption/evacuation cycle at ambient temperature; (iv) reference spectrum, relative to the water vapour adsorption/evacuation at ambient temperature onto a bare A573 sample

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Fig. 9 Absorbance IR spectra obtained in the spectral ranges of pyridine 8a-8b 'ring' modes ($1650-1550 \text{ cm}^{-1}$) and pyridine 19b mode ($1470-1420 \text{ cm}^{-1}$) by pyridine adsorption/evacuation at ambient temperature on various AIF₃ samples, as indicated by the symbols on the curves. (i) Spectrum run after admitting *ca.* 8 Torr pyridine; (ii) same as (i) after subtraction of the spectral contribution due to the physisorbed (liquid-like) pyridine phase (py-ph); (iii) spectrum run after pyridine evacuation for 2 min; (iv) spectrum run after pyridine to 15 min

ascribed above to the desorption of coordinated H_2O from surface AI_{cus}^{VI} sites, does not seem to produce new pyridine adspecies nor any appreciable increase of the overall activity towards pyridine: Curves I and II of Fig. 8 show that in the 300–423 K temperature interval over 60% of coordinated water is desorbed, but very few changes are produced in the spectrum of adsorbed pyridine. This indicates conclusively that very little (if any) activity towards pyridine is due to AI_{cus}^{VI} centres that are created upon vacuum thermal desorption of undissociated coordinated water.

The Brønsted acidity of preparation A (preparations B and C behave very similarly in this respect) is low on highly hydrated samples [see curves I and II, and the bands marked (py-B)], and decreases rapidly with dehydration at T > 450 K [see curve III (i)]. This means that on these systems the strongly acidic surface OH groups needed to yield pyH⁺ ions are very few on the starting material and are eliminated in the early stages of dehydration. Rehydrated samples, which then undergo a second dehydration, behave much as the starting samples in terms of Brønsted activity, implying that irreversible modifications of the surface layer brought about by activation at temperatures as high as 623 K do not appreciably affect the concentration of sites that are capable of yielding surface pyH⁺ ions. A stronger Brønsted activity is observed, however, if an activated sample (e.g. sample A573)

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of curves III) is first contacted with pyridine [trace III(i)] and is then rehydrated at ambient temperature [trace III(ii)]. The amount of coordinated water thus obtained is somewhat lower than it would be in the absence of pre-adsorbed pyridine [*i.e.* some of the relevant sites are inaccessible; compare traces III(ii) and III(iv)], but the surface concentration of pyH⁺ species thus produced is higher and is unchanged by introducing more pyridine [compare III(ii) and III(iii)], as shown by the bands of (py-B) at *ca.* 1640 and *ca.* 1550 cm⁻¹ and by the relative intensity of the bands at *ca.* 1490 and *ca.* 1450 cm⁻¹.³⁰ This implies that the development of an appreciable Brønsted activity at the surface of AlF₃ is attained only by the creation of a high degree of hydration 'on top' of a high concentration of pre-chemisorbed pyridine; in any event, the Brønsted proton activity of AlF₃ is never very high.

As for the various types of adsorbed pyridine, they are shown and discussed in Fig. 9. The figure reports, in the range of the 8a–8b 'ring' modes (1650–1550 $\rm cm^{-1})$ and 19b 'ring' mode of pyridine (1470-1420 cm⁻¹),³¹ the spectra of pyridine adsorbed on some samples A (equivalent, in this respect, to samples B) and samples C. As already suggested by Fig. 8, several pyridine adspecies are formed, and their spectral features can be distinguished and summarized as follows. A first pyridine species, observed only in the presence of a relatively high pyridine pressure, has the 8a-8b modes almost unresolved at ca. 1580 cm^{-1} (superimposed on the unresolved envelope of the 8b modes of all pyridine adspecies), the (1 + 6a) combination mode at ca. 1595 cm⁻ (superimposed on the 8a mode of another pyridine adspecies, described below), and the 19b mode at ca. 1438 cm⁻¹ (well resolved from all other 19b modes). This pyridine adspecies is typically a physically adsorbed one [liquid-like pyridine, (pyph)] and its computer band subtraction (quite easy in the 19b range, more difficult in the 8a-8b range), allows the observation with maximum intensity (i.e. under a high pyridine coverage) of other weakly chemisorbed pyridine species, whose chemisorption is partly reversible upon evacuation of pyridine. This aspect of the spectral features of adsorbed pyridine has been discussed in general terms elsewhere.³²

A second pyridine adspecies exhibits the 8a mode at ca. 1620 cm⁻¹ on both samples A and C (sharper in the latter case), and the 19b mode at ca. 1450 cm⁻¹. It is present in small amounts on A and C samples activated at ambient temperature, but it exhibits stronger and broader bands on samples A activated at T > 450 K, whereas it remains virtually unchanged on samples C. This pyridine species is strongly held, as its bands do not lose intensity when pyridine is evacuated, and in some cases increase somewhat and shift towards higher $\tilde{\nu}$ [see, for instance, the spectra of A573(r)300]. On the basis of data reported in the literature,¹⁶ this species is thought to be pyridine Lewis-coordinated onto (strong) Al_{cus}^{IV} centres [(py-L)_{Aliv}], *i.e.* onto tetrahedrally coordinated (and thus coordinatively defective in respect of the AlF₃ structure) sites located in the surface layer where, after an evacuation at 300 K, they already possess coordinative vacancies capable of coordinating pyridine. In this respect, pyridine is more sensitive in revealing Al^{IV}_{cus} sites than the other probe molecules discussed above, especially in the case of samples C, where these sites were thought to be virtually absent, especially in the high hydration stages.

Finally, there is a third pyridine species, whose 8a mode absorbs at 1595–1600 cm⁻¹ and whose 19b mode is at *ca*. 1445 cm⁻¹. This species is partly reversible upon pyridine evacuation (and thus involves a weak acid–base interaction), and requires a band subtraction of the (py-ph) species to be observed properly with its full intensity. This pyridine adspecies, which dominates the spectra of pyridine adsorbed onto samples activated at low temperatures, declines fast in intensity with increasing activation temperature, and is thus ascribed to the interaction by H-bonding (py-H) with some surface OH groups (this type of interaction was already discussed in Fig. 3). Note that this reversibly H-bonded pyridine species cannot be responsible for the irreversible perturbation of the surface OH band observed on samples A and B at *ca*. 3705 cm^{-1} . This perturbation is more likely due to the interaction of the OH groups (*ca*. 3705 cm^{-1}) with the π -cloud of (some of) the irreversibly bound pyridine adspecies which are strongly Lewis-coordinated onto nearby Al^{IV}_{cus} sites. The weakly held (py-H) species must involve H-bonding of the surface OH groups that absorb at lower \tilde{v} (*i.e.* the OH groups whose stretching mode is superimposed on the strong band(s) due to OH groups in the bulk, and can be evidenced by D₂O exchange, as reported in Fig. 3).

The 8a and 19b modes of (py-H) are in the spectral ranges where one would expect to observe the bands of pyridine Lewis-coordinated onto Al_{cus}^{VI} sites, as in the case of α -Al₂O₃.^{18,19,32} Al^{VI}_{eus} sites are presumed to form abundantly upon evacuation of surface-coordinated water and were revealed by the adsorption of CO₂ and (less clearly) by the adsorption of CO at ca. 78 K. No evidence was obtained for the formation of a weak Lewis-coordinated pyridine species with 8a and 19b modes in those spectral ranges, and whose intensity may be thought to depend on the desorption of the abundant surface-coordinated H₂O. This is an apparent contradiction: Al_{cus}^{VI} sites form upon dehydration, but a strong Lewis base like pyridine does not reveal them. The contradiction can possibly be explained by the strong Lewis coordination (starting already from the earliest stages of the dehydration on both samples A and C) of pyridine onto nearby Al_{cus}^{IV} centres; inductive effects from the strong py/ Al_{cus}^{IV} surface complexes would prevent an appreciable formation of the weak $py/Al_{cus}^{v_1}$ complexes, as is sometimes observed with other adsorbates. For instance, in the case of the adsorption of CO_2 on samples A (shown in Fig. 7), the formation of strong CO_2/Al_{cus}^{IV} end-on complexes is observed to induce a decrease in intensity of the band(s) of the weaker CO_2/Al_{cus}^{VI} , which were initially formed at lower dehydration stages. The absence of py/Al_{cus}^{VI} complexes at the surface of AlF₃ implies that cus Al^{v_1} centres are extremely weak as Lewis acidic sites, and is quite strange, considering that even at the surface of transition aluminas (i.e. on a system characterized by the presence of abundant strong pyridine complexes formed at Al^{IV}_{cus} centres,¹⁶ weak activity of Al^{VI}_{cus} sites towards pyridine coordination could be noted.

Conclusions

By means of the *in situ* FTIR spectroscopic technique and the adsorption of suitable test molecules, it has been possible to understand some of the characteristics of different AIF_3 specimens. Although on crystallographic grounds several different AIF_3 phases can be distinguished, the actual crystal phase has very little importance (if any at all) in determining the bulk and surface features of an AIF_3 specimen, whereas appreciable differences are brought about by the preparative procedure. The latter is primarily responsible for the type and amount of bulk and surface impurities and imperfections.

Adsorption experiments demonstrate that all AlF_3 preparations have at the surface variable and appreciable amounts of oxidic islands, even when the material derives from (nominally) non-oxygen-containing precursors. The term 'nominally' refers to the fact that water in some form is unavoidably contained in any precursor of the AlF_3 preparations. Adsorption experiments also demonstrate that a large fraction of the oxidic islands are at the surface of the material, and not merely contained in the bulk of the

material as cores of unreacted alumina, as is often reported for AlF_3 preparations derived from the direct fluorination of Al_2O_3 . Preliminary data concerning the physical/chemical features of AlF_3 -supported metal catalysts (to be described elsewhere) indicate that surface oxidic islands play an important role. In fact, the grafting process and the dispersion properties of the supported-metal moiety are related in a complex way to the nature and location of the oxidic islands originally present on the support.

The surface oxidic islands contain different types and variable amounts of OH groups and of 'anomalous' Al cationic centres with a (quasi-)tetrahedral coordination, *i.e.* surface species normally observed on transition aluminas. Still, the overall behaviour of the surface oxidic islands is different from that of the various Al_2O_3 transition phases: in fact OH groups and Al^{IV} sites in the islands are unstable with respect to vacuum thermal treatments at relatively low temperatures, whereas this is not the case for alumina(s).

Most of the surface activity exhibited by AIF_3 is ascribed to the presence of the surface oxidic islands and, in the case of preparations from $(NH_4)_3AIF_6$, of surface NH_x species. The surface of the 'regular' AIF_3 network is unreactive. In particular, surface cus AI^{VI} centres, created by vacuum elimination of coordinated molecular water, possess a very low Lewis acidity (even lower than on α - Al_2O_3), and their presence is difficult to discern by adsorption of the usual probe molecules.

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