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Infrared Study of the Adsorption of Pyridine on α-Al_2O_3

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The adsorption and desorption of pyridine has been studied on two preparations of α-Al_2O_3, obtained by thermal treatment of γ-Al_2O_3 for different times. Although the X-ray diffraction spectra of the two are indistinguishable and correspond to a pure α-Al_2O_3 phase, remarkable differences are observed in the surface behavior. These differences are ascribed to the existence at the surface of small and variable amounts of Al ions still possessing a tetrahedral or quasi-tetrahedral coordination. These centers bring about the formation of two Lewis coordinated pyridine species, both with the 8a mode at $\tilde{\nu} > 1610$ cm^{-1}, on the material heat-treated for the shorter time, and of one such species on the oxide treated for the longer time. On both preparations another Lewis coordinated Py species is predominant, with the 8a mode at $\tilde{\nu} \cong 1596$ cm^{-1}, i.e., at the same frequency as pyridine H-bonded to surface OH groups via the N lone pair and assigned to centers involving octahedrally coordinated Al ions. The overall pyridine coverage is fairly low on both materials ($\leqslant 20\%$ at a pressure of ~ 8 Torr), while the concentration of defective centers able to coordinate pyridine is found to be between 0.5 and 1.0/nm^2.

INTRODUCTION

Samples of α-Al_2O_3 suitable for spectroscopic work have been prepared by treating a transition alumina of high external surface area already in the form of ir pellets at 1150°C. The time of treatment was observed to play a relevant role in determining the surface area, although no differences were ever observed in the X-ray diffraction spectra, and electron microscopy revealed the presence of hexagonal platelets of variable radius and very small height in each preparation. The bulk properties of the solid point toward the existence, in every case, of a well-crystallized phase in which the (0001) face is definitely predominant. Previous ir work (*1–3*), on the other hand, showed that remarkable differences of surface behavior can be observed as a function of treatment time. Two preparations were usually used, termed α-12 and α-22 (heated for 12 and 22 hr, respectively) and thus short- and long-treated samples.

Previous results can be summarized as follows:

(1) No carbon monoxide chemisorbs on either preparation (*1*), indicating that no strong Lewis acidity exists on α-Al_2O_3. In view of the previous assignment (*1*) of strong Lewis acidity at the surface of aluminas to tetrahedrally coordinated Al (Al^{IV}), this datum seems consistent with the expected complete transformation of Al^{IV} into octahedral Al (Al^{VI}).

(2) The spectra of surface hydroxyls and the dehydration patterns of the two preparations are fairly different (*2*), the shorter-treated one exhibiting some OH groups (free OH groups absorbing at 3756 and

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3692 cm^{-1} and H-bonded groups at $\sim$3567 cm^{-1}, respectively) that are missing on the other sample and are typical of transition aluminas. This fact has been ascribed to the existence of some Al ions still exhibiting, or simulating, a tetrahedral coordination.

(3) The chemisorption of CO_2 (*3*) confirms the existence of some Al ions of anomalous coordination on the α-12 sample, mainly through the formation on this preparation of surface bicarbonates that are entirely missing on longer-treated samples and are, on the contrary, very common in all transition phases (*4*).

The present work deals with the chemisorption of pyridine (Py), and its aim is twofold. On the one hand, by the use of a hard base we hope to be able to solve the contradiction between the behavior of CO and that of CO_2 and surface hydroxyls. In fact, the existence of some residual tetrahedral coordination on α-12 could yield some Lewis acidity strong enough to coordinate Py. On the other hand, the use of an Al oxide with a simpler cationic coordinative situation than in the case of transition aluminas should throw some light on the nature of the various Py species adsorbed on the latter oxides. In this respect we recall that several papers have already been devoted to the interaction of Py with transition aluminas and that the relevant results have been recently reviewed by Knözinger (*5*). It may be noted that there is a certain disagreement among authors concerning both the assignment and the correlation between the Py bands, and we take this up in the Discussion.

EXPERIMENTAL

All details concerning sample preparation and characterization, instrumentation and instrumental conditions, and the spectral deconvolution technique have been reported elsewhere (*2*). Let us merely recall that we term α-12 and α-22 two α-Al_2O_3 preparations obtained by heating γ-Al_2O_3 at 1150°C in the air for 12 and 22 hr, respectively, and that the two specimens have surface areas of 25 and 16 m^2 g^{-1}, respectively. High purity grade Py was always distilled *in vacuo* before use. α-Al_2O_3 samples were activated at the desired temperature and cooled to room temperature before admission of Py. No heating in the presence of Py vapor was ever performed, while Py desorption was carried out each time at higher and higher temperatures.

RESULTS

α-12: The 1425–1635 cm^{-1} Range

This is the range where several Py "ring" modes occur, termed 19b, 19a, 8b, and 8a, according to Kline and Turkevich (*6*) and which are known as "the most sensitive vibrations, especially modes 8a and 19b, with regard to the nature of intermolecular interactions via the nitrogen lone pair electrons" (*5*).

Figure 1 shows the spectra of α-12 dehydrated at 100°C on which Py was adsorbed at 8 Torr and subsequently desorbed at increasing temperatures. Figure 2 refers to α-12 dehydrated at 850°C. It is noted that:

(1) Py evacuation at room temperature causes several changes, the most relevant being the elimination of a species, referred to as Py_1, with modes at $\sim$1442, 1484, 1574 (shoulder), and 1583 cm^{-1}. This species is strongly dependent on Py pressure and is assigned to Py perturbed by a very weak field, so that its spectral features are nearly coincident with those of the liquid phase (*7*). It is difficult to decide whether Py_1 is due to an extremely weak specific interaction with coordinating sites or to a nonspecific interaction (i.e., to physically adsorbed Py), as we have no idea of the Py p/p_0 value at the temperature of the ir beam. Owing to the uncertain assignment, Py_1 is not dealt with in detail in the text.

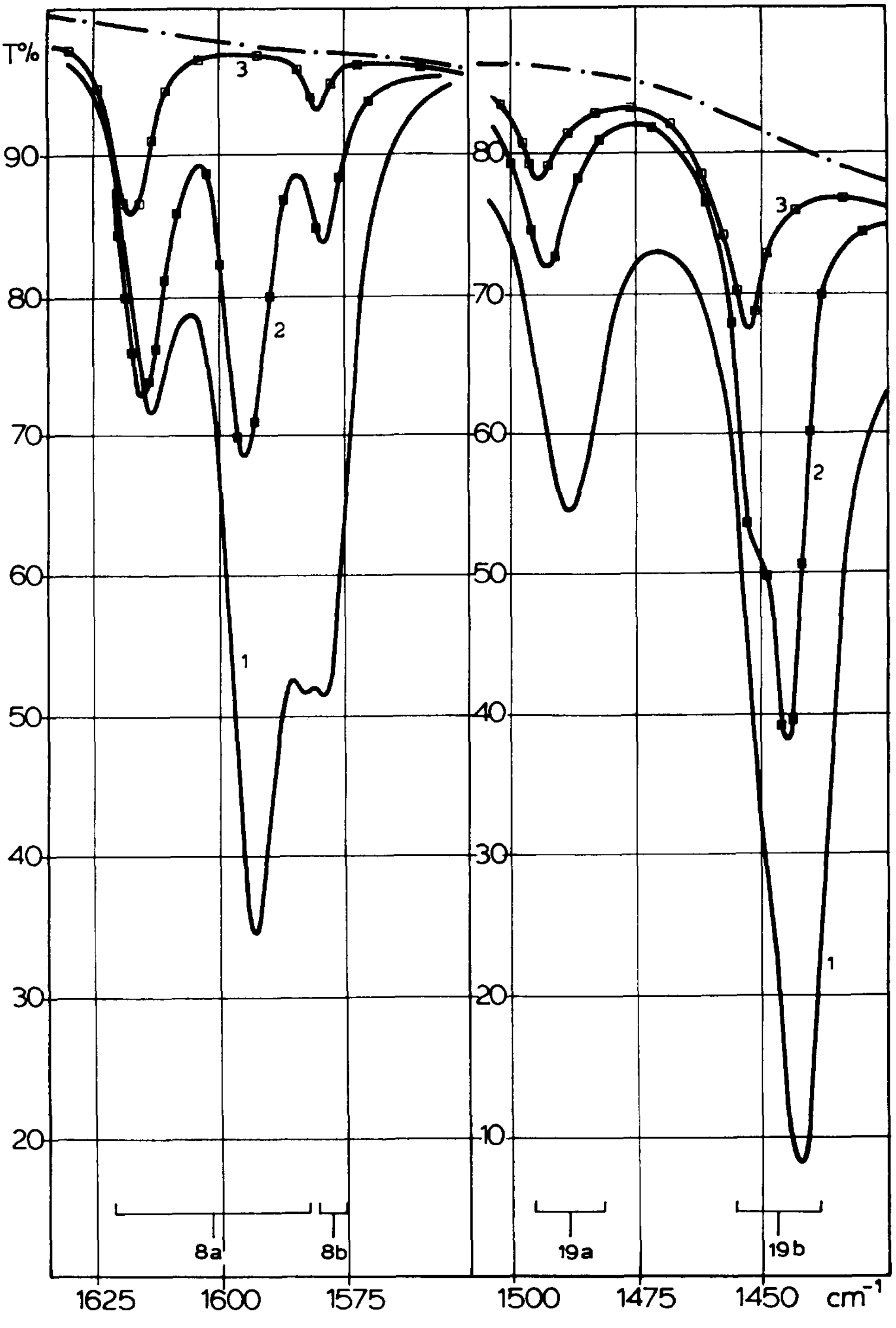


FIG. 1. Infrared spectra in the 1425 to 1635 cm^{-1} range of Py interaction with α-12 dehydrated at 100°C. —·—, background; 1, ——, 8 Torr Py added; 2, -■—■—■-, Py evacuated at 25°C; 3, -□—□—□-, Py evacuated at 100°C.

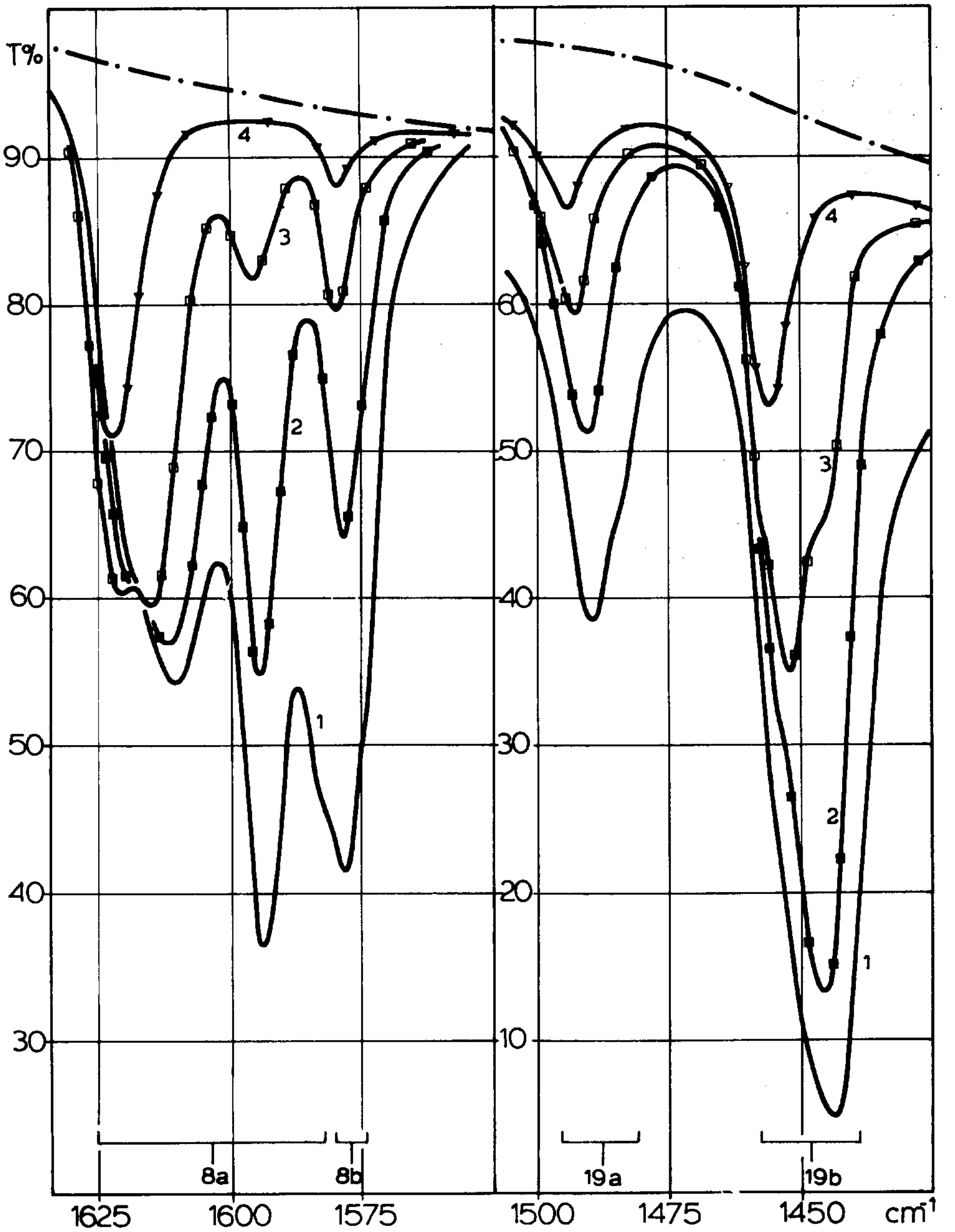


FIG. 2. Infrared spectra in the 1425 to 1635 cm^{-1} range of Py interaction with α-12 dehydrated at 850°C. —·—, background; 1, ——, 8 Torr Py added; 2, -■—■—■-, Py evacuated at 25°C; 3, -□—□—□-, Py evacuated at 100°C; 4, -▽—▽—▽-, Py evacuated at 200°C.

(2) After the elimination of Py_1, no discrete components are evident in modes 8b and 19a upon further Py desorption, the former band being nearly constant at 1580 cm^{-1} and the latter exhibiting a gradual shift to higher wavenumbers.

(3) Modes 19b and 8a reveal the existence of two other species on the sample

activated at 100°C, termed Py_2 and Py_3 in order of increasing frequencies, and of an additional species, termed Py_4, on the sample activated at 850°C. Py_4 is characterized by the highest 8a and 19b components.

(4) The various 19b modes are reasonably well resolved (which is not the case with transition aluminas due to the intensity) and are fairly constant in frequency and width both with coverage and with sample dehydration temperature. Mode 19b frequencies are: 1445, 1452, and 1456 cm^{-1} for Py_2, Py_3, and Py_4, respectively.

(5) Mode 8a, by far the most sensitive, is of very variable frequency and width both with coverage and with sample pretreatment temperature. Therefore, the 1550 to 1635 cm^{-1} range was chosen as the analytical one and was computer-resolved, with a suitable program previously described (*2*), on samples dehydrated at various temperatures. All 8a peaks were best fitted by Gaussian curves, consistent with their variable and likely composite spectral characteristics, while the unresolved 8b mode was equally well simulated with either a Gaussian or a Lorentzian curve.

All spectra were resolved individually, even though our program also allows the simultaneous deconvolution of several spectra, due to the variable position and width of some bands with sample activation temperature and with Py evacuation temperature. The number of bands in terms of

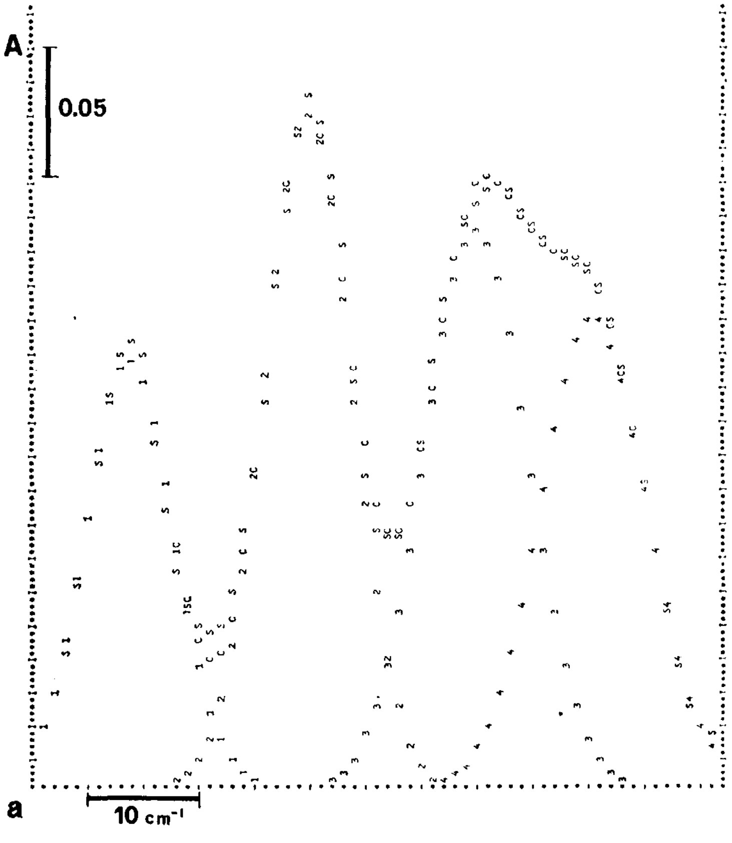
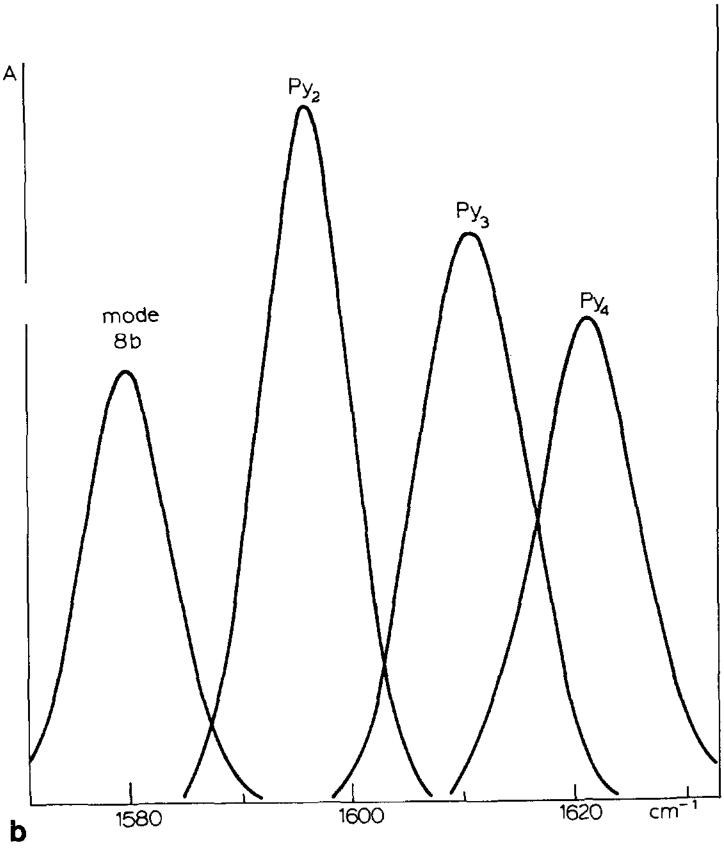


FIG. 3. (a) Spectral simulation and deconvolution of the 1572 to 1633 cm^{-1} range of α-12 dehydrated at 850°C on which Py was adsorbed and pumped off at 25°C. The frequency scale is reversed with respect to Fig. 2. S, experimental curve; C, calculated curve. (b) Reproduction of the bands computer-resolved in (a).



which the resolution was carried out, was fixed in each case on the basis of the number of observable maxima. Peak position and width were always floating parameters.

The spectra run in the presence of 8 Torr Py were deconvoluted only from 1587 cm^{-1} upward, i.e., assuming that no other bands existed below this frequency. This assumption certainly overestimated somewhat the integrated absorbance of Py_2 (8a mode at $\sim$1594 cm^{-1}), but the error was much lower than in any trial where mode 8b was also deconvoluted when in the presence of considerable amounts of the weakly held Py_1.

The deconvoluted spectrum of α-12 dehydrated at 850°C, on which Py was adsorbed and evacuated at room temperature, is shown in Fig. 3.

Table 1 summarizes the characteristics of all bands, as obtained through the spectral deconvolution. It can be seen that:

(1) Band 8b is fairly constant in position, but not so much in width. In fact it becomes sharper on decreasing Py coverage and on increasing sample activation temperature. This is thought to follow from the variable number and concentration of different chemisorbed species whose 8b bands coincide at nearly the same frequency.

(2) Mode 8a of Py_2 is quite constant in width and grows only moderately in frequency on increasing the activation temperature.

(3) Py_3 and Py_4 have the 8a mode very variable in both position and width, with a well-defined dependence on sample dehydration temperature.

(4) All 8a modes have frequencies that are very sensitive to the Py coverage.

In particular, the frequency increases as the Py coverage decreases, such that upon Py evacuation at room temperature a band-crossing is consistently observed, as shown by Figs. 1 and 2. This simulates an increase of Py_4 concentration with increasing Py desorption temperature, which is not confirmed by the deconvolution (see Fig. 4), and is merely due to the band (of unchanged or even slightly decreased intensity) moving to higher frequencies with decreasing concentration of other Py species.

Figure 4 is a plot of the activation temperature versus the integrated absorbance for mode 8b and all 8a modes as obtained after Py evacuation at 25°C (A) and 100°C (B). Figure 4A shows that Py_2 exhibits a peculiar trend: It possesses a maximum for activation at 100°C, a deep minimum at 400°C, and another maximum after activation at 600 to 700°C. Py_3 concentration grows for dehydration in the 25 to 400°C range and then remains almost constant, with a minor decrease in the 600 to 850°C interval. Py_4 is absent on samples dehydrated below 200°C, after which it grows with continuity. From Fig. 4B (Py desorbed at 100°C) it is seen that the behavior of Py_3 and Py_4 is unchanged, a definitely higher fraction of the former species being desorbed. As for Py_2, there remains only a small fraction of the amount adsorbed on highly dehydrated samples. Finally, the points and arrows on the right-hand side of Fig. 4B show the amounts of the three chemisorbed species remaining after a further Py evacuation at 200°C (spectrum 4 of Fig. 2).

α-12: The 3300–3800 cm^{-1} Range

This is the range of surface OH groups, whose characteristics have been dealt with elsewhere (*2*). Figure 5 shows the spectral changes produced in this range upon Py adsorption, and subsequent desorption, on a highly hydrated sample (A) and on a medium hydrated one (B). As no surface OH groups remain on α-12 after dehydration at $T \geqslant 800°C$, no spectra in this range are reported relative to the adsorption of Py on the sample dealt with in Fig. 2. Figure 5 shows that:

(1) All OH bands are perturbed by Py adsorption, new ill-defined maxima appearing at 3720, 3675, 3550, 3500, and 3340 cm^{-1}.

(2) On highly hydrated samples (Fig. 5A), Py evacuation below 100°C fully restores the OH spectrum, while on more dehydrated samples (Fig. 5B) higher Py evacuation temperatures are needed to obtain the starting OH spectrum. This suggests that all chemisorbed Py species may perturb nearby surface hydroxyls through a π-cloud H-bonding, and that Py_4, when present, certainly interacts with them.

(3) Of the various free OH species, the highest absorbing one (3756 cm^{-1}) is restored last on Py desorption and is thus probably perturbed by Py_4.

(4) Figure 5B, as well as the spectra of more dehydrated samples (not shown in the figure), indicate that the original OH spectrum is always restored after Py desorption, so that the reaction recently observed by Knözinger *et al.* (*5, 8*) on transition aluminas leading to the formation of α-pyridone at the expense of some high $\bar{\nu}$ surface hydroxyls is excluded at the surface of α-12.

α-22: The 1425–1635 cm^{-1} Range

The same spectral analysis and computer deconvolution reported above for α-12 have been carried out on the spectra of Py adsorbed on α-22. Figure 6 shows the spectra relative to an α-22 sample dehydrated at 700°C, i.e., fully dehydroxylated (see Fig. 2 of Ref. *2*), and thus, comparable to the spectra in Fig. 2. No spectra are reported relative to less dehydrated samples as the

TABLE 1

Spectral Positions and Half-bandwidths (cm^{-1}) of Modes 8a and 8b of Various Py Species Adsorbed on the Surface of α-12 at Various Coverages

Band	$\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$[a]			
	P_{Py} = 8 Torr	After Py, evacn, 25°C	After Py, evacn, 100°C	After Py, evacn, 200°C
8b All species	Not evaluated	1580	1580	1580
		13–10	11–8	8–7
8a, Py_2	1594	1596	1597–1598	No such
	9–10	10	10–11	band remains
8a, Py_3	1612–1609	1616–1611	1619–1615	1618–1615
	14	13–11	12–10	10–9
8a, Py_4	1623–1620	1625–1621	1627–1623	1626–1624
	12	11–12	9–10	10

[a] Frequency and bandwidth ranges show the trend exhibited with increasing dehydration temperature of the sample.

same bands are observed, though with different relative intensities. Table 2 reports the characteristics of modes 8b and 8a coming from the spectral deconvolution, and Fig. 7 plots the integrated absorbances of modes 8a and 8b after Py desorption at ambient temperature against a few selected dehydration temperatures. Points

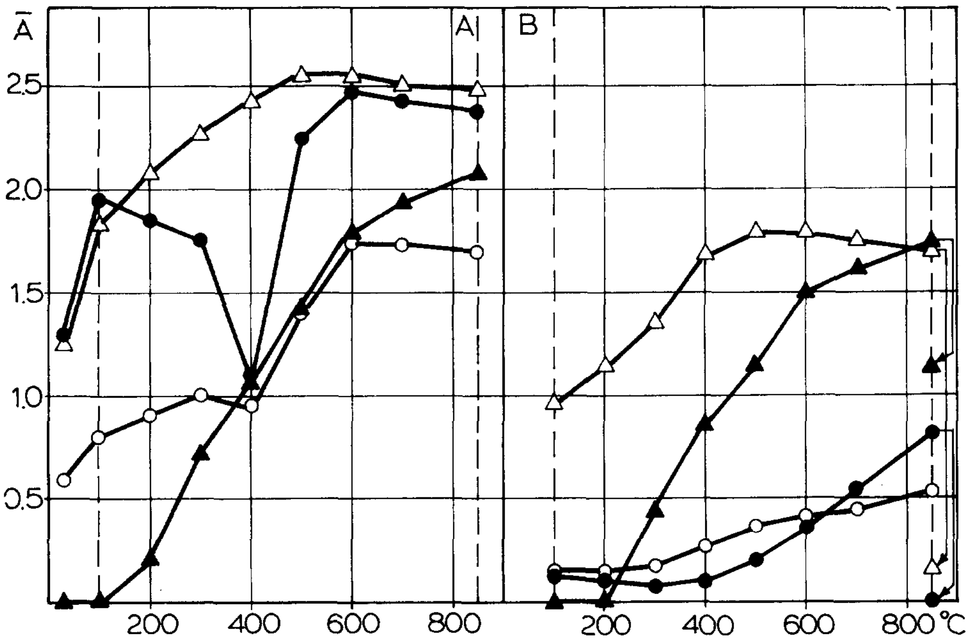


FIG. 4. Integrated absorbance of various Py modes as a function of α-12 dehydration temperature. (A) after Py evacuation at 25°C. (B) After Py evacuation at 100°C. -○—○—○-, mode 8b at 1580 cm^{-1}; -●—●—●-, mode 8a at 1596 cm^{-1} (Py_2); -△—△—△-, mode 8a at 1616 cm^{-1} (Py_3); -▲—▲—▲-, mode 8a at 1623 cm^{-1} (Py_4). The broken vertical lines indicate the integrated intensities of the bands of Figs. 1 and 2 (curves 2 in A and curves 3 in B).

and arrows on the right-hand side of the plot show what remains of the various adsorbed species after Py evacuation at 100°C (spectrum 3 of Fig. 6). No Py remains after a 200°C evacuation.

It is observed that:

(1) The overall intensities of the α-22 spectra are lower than in the case of α-12 to an extent that cannot be ascribed solely

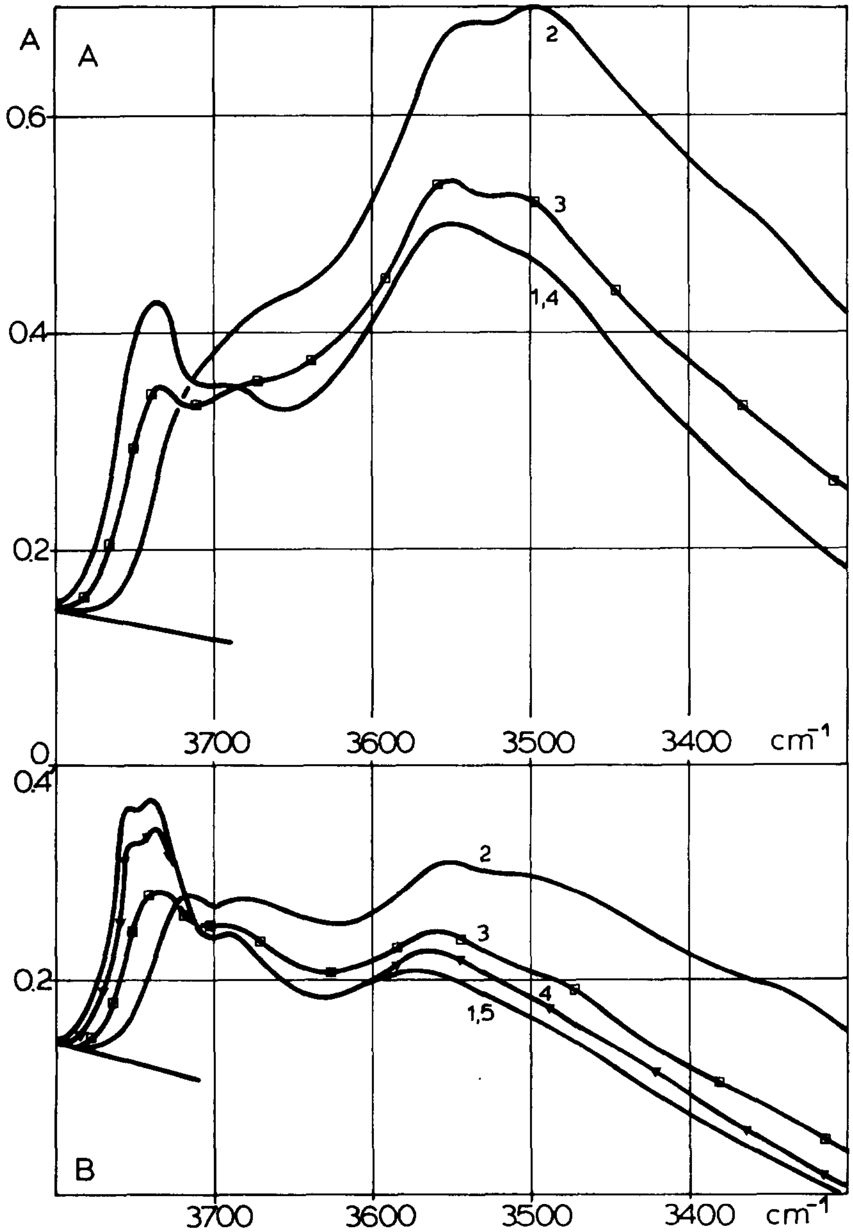


FIG. 5. Infrared spectra in the 3300 to 3800 cm^{-1} range of Py interaction with α-12 dehydrated at 100°C (A) and at 300°C (B). 1, background. 2, 8 Torr Py added; 3, after Py evacuation at 25°C; 4, after Py evacuation at 100°C; 5, after Py evacuation at 200°C.

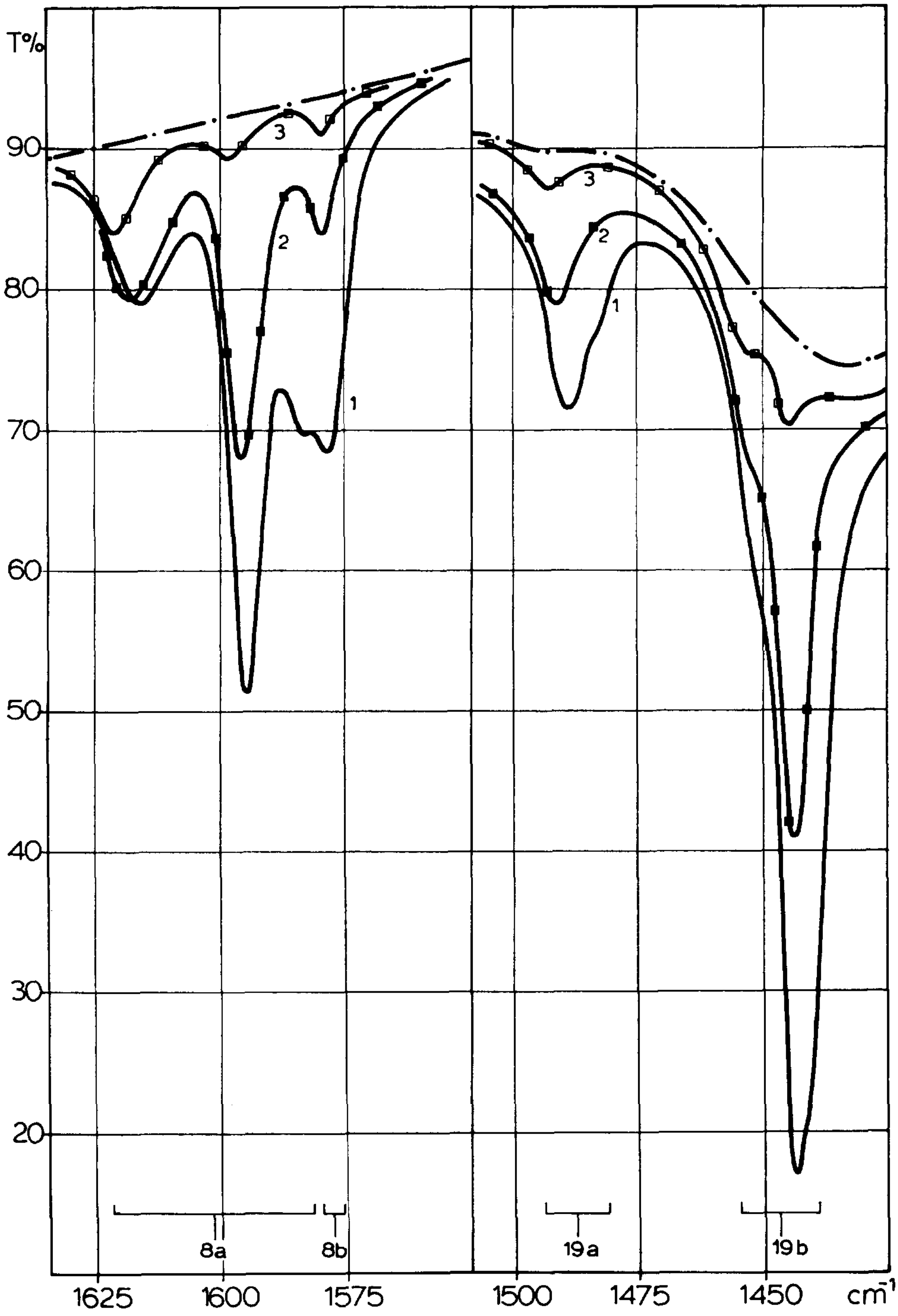


FIG. 6. Infrared spectra in the 1425 to 1635 cm^{-1} range of Py interaction with α-22 dehydrated at 700°C. —·—, background; 1, ——, 8 Torr Py added; 2, -■—■—■-, Py evacuated at 25°C; 3, -□—□—□-, Py evacuated at 100°C.

to the lower surface area. In fact, sample weights were such as to give, in the case of an equal concentration of surface-active species and of constant extinction coefficients, an intensity ratio of ~1.3 between α-12 and α-22, and such a ratio is only roughly exhibited by the Py_2 species.

(2) The behavior of modes 8a and 8b of Py_2 (Table 2 and Fig. 7) shows that, apart from a minor difference of half-bandwidth and a slightly lower resistance to desorption, this species corresponds well with the Py_2 species of α-12. The minimum of Py_2 concentration is still observed, though at a somewhat lower dehydration temperature than on α-12.

(3) On α-22 there is only one Py species (Py_3) whose 8a mode lies above 1600 cm^{-1}. Py_3, though more similar to Py_3 than to Py_4 of α-12 in terms of thermal resistance, exhibits the width and position of mode 8a and an intensity trend on dehydration temperature intermediate between the two high-frequency bands of α-12. The position of mode 19b, on the contrary, coincides with that of Py_3 on α-12.

α-22: The Surface OH Region

No spectra are reported relative to this spectral range, as the results of α-22 are all consistent with those previously discussed for α-12. In particular, the original surface OH spectrum is fully restored upon Py evacuation at 100 to 200°C, and the high-frequency flank of the only free OH band (absorbing at 3733 cm^{-1} (*2*)) is restored last. The reaction transforming Py_{ads} into α-pyridone is thus excluded also on α-22.

TABLE 2

Spectral Positions and Half-Bandwidths (cm^{-1}) of Modes 8a and 8b of Various Py Species Adsorbed on the Surface of α-22 at Various Coverages

Band	$\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$[a]		
	P_{Py} = 8 Torr	After Py, evacn, 25°C	After Py, evacn, 100°C
8b, All species	Not evaluated	1581	1581
		15–14	15–14
8a, Py_2	1595	1596	1596–1597
	8	8	8
8a, Py_3	1613–1615	1615–1618	1615–1618
	18–22	17–19	17–19

[a] Frequency and width ranges show the trend exhibited with increasing dehydration temperature of the sample.

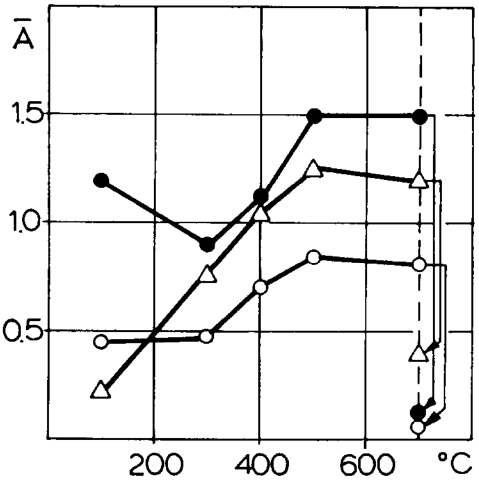


FIG. 7. Integrated absorbance of various Py modes as a function of α-22 dehydration temperature, after Py evacuation at 25°C. –○—○—○–, mode 8b at 1581 cm^{-1}; –●—●—●–, mode 8a at 1596 cm^{-1} (Py_2); –△—△—△–, mode 8b at ~1618 cm^{-1} (Py_3). The broken line indicates the integrated intensity of the bands of Fig. 6, curve 2.

Quantitative Data

The chemisorption of Py on fully dehydrated α-12 and α-22 has been also studied with a vacuum microbalance, and relevant data are reported in Table 3. No data are reported relative to the chemisorption in the presence of a Py pressure, as the physically adsorbed phase, quite abundant at the temperature at which the microbalance operates, and its variable amount due to temperature fluctuations, made the weight reading not very reliable.

DISCUSSION

Assignment

The assignment of Py species chemisorbed on α-Al_2O_3 can be made somewhat easier with the aid of the assignment of Py species at the surfaces of transition aluminas (*5*, *9*). Figure 8 shows the spectra in the 1425 to 1635 cm^{-1} range of Py chemisorbed at various coverages on θ-Al_2O_3 dehydrated at 700°C and still possessing some 10% surface OH groups. θ-Alumina was chosen as it represents the last step of the phase transformation of one of the Al hydrates into α-Al_2O_3 along the pathway bayerite $\rightarrow \eta \rightarrow \theta \rightarrow \alpha$. The pattern of spectra closely resembles that of α-12 dehydrated at 850°C (Fig. 2) but for a higher overall intensity and a fairly different intensity ratio among various species, most clearly seen in the mode 8a region. Neglecting physically adsorbed Py, if any, it is almost universally accepted that, on transition aluminas, the high-frequency 8a modes[1] belong to different Lewis coordinated Py species, while the band at ~1600 cm^{-1} is due to the 8a mode of Py molecules interacting with surface OH groups through nitrogen H-bonding. The latter assignment is mainly based upon the behavior of the Py/SiO_2 system, on which only the H-bonding interaction takes place if SiO_2 is dehydrated below ~700°C, and on the intensity trend exhibited by the ~1600 cm^{-1} band with surface OH group concentration.

It is quite evident that such an assignment is unable to explain some of the present results: In fact, there are two maxima in the intensity plot of the 1596 cm^{-1} band (Py_2) in Figs. 4 and 7. Moreover, the spectra of Figs. 2 and 6 refer to fully dehydrated samples. The 1596 cm^{-1} band, which was treated as due to a single Py species on the basis of its spectroscopic features, must be thus assigned to two different Py species of fairly similar spectral characteristics and resistance to evacuation but characteristic of different dehydration stages. The species prevailing at high surface OH concentrations, and responsible for the first maximum in the Py_2 plot of Figs. 4 and 7, is thought to be an H-bonded Py, as in the case of transition aluminas, while the species prevailing at high dehydration stages must be ascribed to a Lewis coordinated Py, whose sites are created upon water desorption below 600°C. The minimum in the Py_2 plot occurs at a lower temperature on α-22 than on α-12, consistent with the easier dehydration of α-22 (*2*). As the Py_2 Lewis coordinated species is peculiar to α-Al_2O_3, it is thought to involve the octahedral coordination alone of Al ions, although the actual nature and structure of the site is still unknown. In fact an Al^{VI} ion could be involved, with one or more coordination vacancies, or a group of more Al^{VI} ions. The assignment of a band at 1596 cm^{-1} to the 8a mode of a Py species coordinated to octahedral cation(s) is consistent with previous observations on $MgAl_2O_4$ and on MgO (*10*). As far as the coordinated species with 8a modes above 1610 cm^{-1} are concerned, they are definitely predominant on θ-Al_2O_3, as well as on all other transition aluminas. On passing to the α-phase, there are still two distinct species (Py_3 and Py_4) on the short-treated α-12 specimens, comparable in in-

TABLE 3

Py Chemisorbed (Molecules per nm^2) on the Fully Dehydrated Surface of α-12 and α-22 at Various Coverages

Py evacuation temperature (°C)	α-12 (dehydrated at 850°C)	α-22 (dehydrated at 700°C)
25	1.13	1.14
100	0.59	0.17
200	0.17	—

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[1] The range of the high-frequency 8a modes is 1632 to 1610 cm^{-1}, in which one to three different Py species have been identified by various authors (*5*).

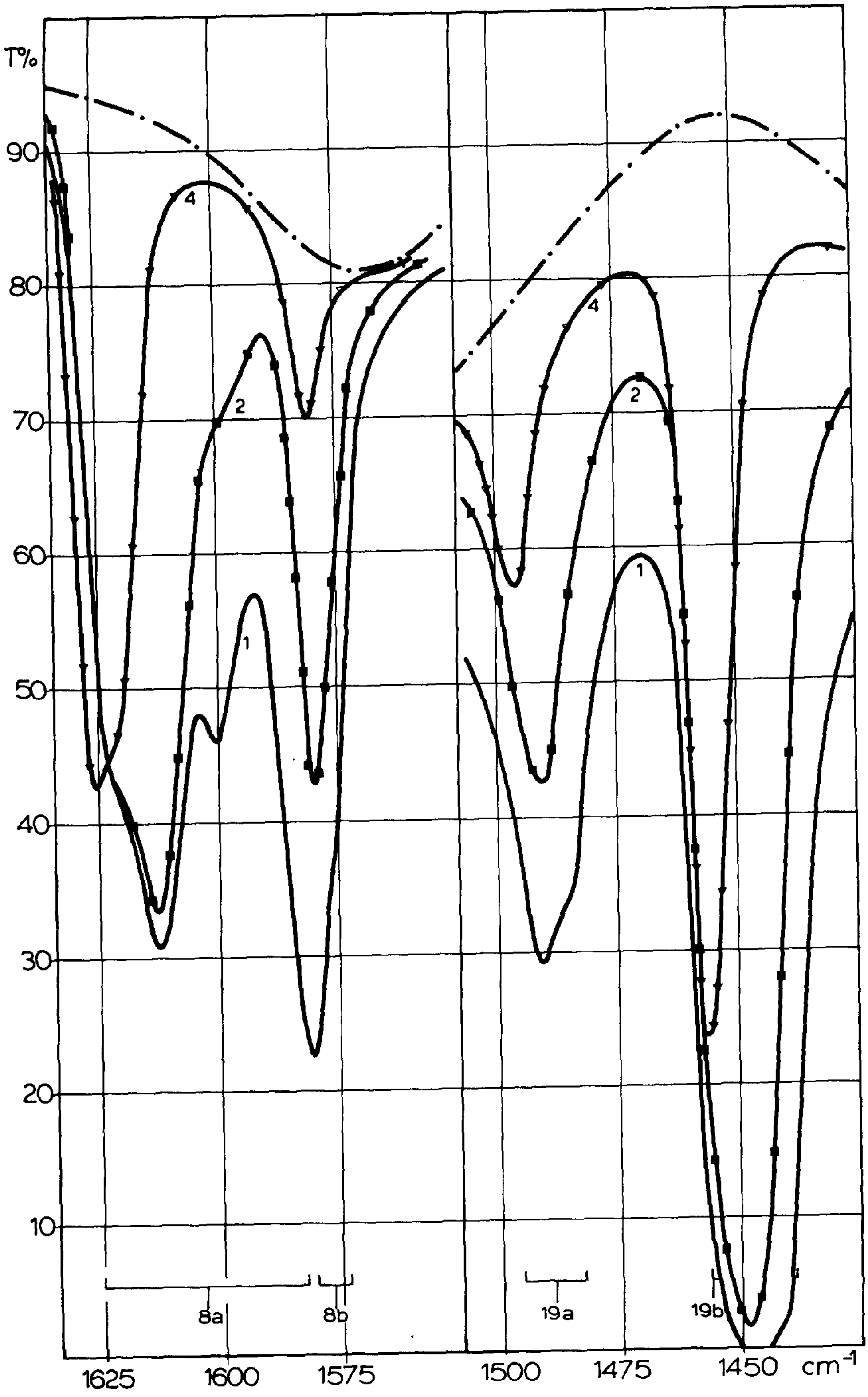
T%
90
80
70
60
50
40
30
20
10
4
2
1
4
2
1
8a
8b
19a
19b
1625
1600
1575
1500
1475
1450
cm-1

FIG. 8.

tensity to Py_2, while there is only one species (Py_3) of definitely lower intensity than Py_2 on the long-treated α-22 specimens. This suggests that:

(1) The coordinated species, whose 8a mode is above ~1610 cm^{-1}, are peculiar to the transition phases and most likely involve tetrahedrally coordinated Al ions. The actual nature of the two sites will be dealt with elsewhere.

(2) Two types of Lewis acidic centers involving Al^{IV} ion(s) still exist at the surface of α-12, confirming the incomplete transformation of Al^{IV} into Al^{VI} at the surface of this preparation (*2*, *3*).

(3) Most unexpectedly, the longer-treated preparation also still possesses some strong Lewis acidic sites involving tetrahedral or quasi-tetrahedral Al ions, although in smaller amounts (at least on the basis of the ir intensity) and with modified characteristics compared to α-12. Other α-Al_2O_3 samples obtained through longer thermal treatments or through treatments at higher temperatures were also found to exhibit minor amounts of coordinated Py with the 8a mode above 1610 cm^{-1}. This agrees with the observation that α-Al_2O_3 catalysts always exhibit to some extent parasite reactions characteristic of transition aluminas, for which Al^{IV} ions are most probably responsible (*1*, *4*).

Quantitative Aspects of Py Adsorption

It was previously shown (*2*) that the dehydration of α-Al_2O_3 in the 25 to 850°C range brings about the complete dehydroxylation and the elimination of some 7.5 water molecules/nm^2 of surface, which should leave an equal amount of coordinated unsaturated (cus) cations at the surface. Moreover, appreciable amounts of Py already coordinate at the surface of a sample activated at room temperature (see Fig. 4), i.e., before the elimination of those ~7.5 water molecules has begun, so that, after the complete dehydration, more than 7.5 cus cations/nm^2 should exist at the surface. A figure of this order is also arrived at if we consider the dehydration of the (0001) face of α-Al_2O_3 (*11*), although the use of such an ideal model is critical in view of the existence of a certain amount of "anomalous" cationic centers. The data of Table 3 show that the overall Py uptake is fairly low.

It is now necessary to give our results a more quantitative meaning so that we may find the answers to the following questions:

(1) What is the total concentration of coordinated Py at various dehydration stages and at various Py coverages? It is particularly interesting to check the concentration of more labile coordinated Py species under a high Py pressure (i.e., in the presence of Py_1) to extrapolate the maximum coverage of Lewis coordinated species.

(2) What is the amount of each coordinated Py species necessary to evaluate the minimum concentration of "anomalous" Al^{IV} centers on the two preparations?

Let us refer first to the α-12 preparation, on which more species are involved and many more results are available. If we assume that (1) the extinction coefficient of the 8b mode (band at 1580 cm^{-1}) is the same for all species; (2) the extinction coefficient of the 8a mode at 1596 cm^{-1} is the same for the two Py_2 species (i.e., the one H-bonded to surface OH groups and the other coordinated to Al^{VI} ion(s)); (3) the extinction coefficient of each 8a mode

FIG. 8. Infrared spectra in the 1425 to 1635 cm^{-1} range of Py interaction with θ-Al_2O_3 dehydrated at 700°C. —·—, background; 1, ——, 8 Torr Py added; 2, -■—■—■-, Py evacuated at 25°C; 4, -▽—▽—▽-, Py evacuated at 200°C. Spectrum 3 (Py evacuated at 100°C) is not reported so as not to overcrowd the plot and to show clearly the strong band-crossing occurring in θ-Al_2O_3 on Py evacuation.

does not vary appreciably with the frequency changes observed with coverage and pretreatment condition; and if we term $\bar{A}_{\bar{\nu}}$ the integrated absorbance at wavenumber $\bar{\nu}$, $[\bar{A}]_{\bar{\nu}_i}$ the integral extinction coefficient of the band centered at wavenumber $\bar{\nu}_i$, α_i the ratio $[\bar{A}]_{1580}/[\bar{A}_{\bar{\nu}_i}]$, where $i = 2, 3, 4$ for Py_2, Py_3, and Py_4, respectively, we can write

$$\bar{A}_{1580} = \alpha_2\bar{A}_{1596} + \alpha_3\bar{A}_{1616} + \alpha_4\bar{A}_{1623}. \quad (1)$$

All the data of the Py/α-12 interactions at various dehydration stages and coverages have been computer-correlated and yielded the α_i values.

$[\bar{A}]_{1580}$ can be easily calculated as the adsorbed amounts n_j reported in Table 4 are related to it and to the corresponding $\bar{A}_{1580}$ through the equation:

$$(\bar{A}_{1580})_j = [\bar{A}]_{1580} \times n_j \times \mathbf{a}, \quad (2)$$

where $\mathbf{a}$ is a coefficient that allows for the fact that n_j is expressed in Py molecules/nm^2, while the concentration is, in the Lambert–Beer equation, in mol dm^{-3}.

The three n_j values of Table 3 yielded an average value, $[\bar{A}]_{1580} = (7.5 \pm 0.3) \times 10^2$ cm^{-2} mol^{-1} dm^3, from which the following $[\bar{A}]_{\bar{\nu}_i}$ (in cm^{-2} mol^{-1} dm^3) were evaluated: $[\bar{A}]_{1596} = 29.6 \times 10^2$; $[\bar{A}]_{1616} = 32.0 \times 10^2$; $[\bar{A}]_{1623} = 36.0 \times 10^2$. Similar calculations were also carried out with the Py/α-22 data and yielded the following $[\bar{A}]_{\bar{\nu}_i}$ values (in cm^{-2} mol^{-1} dm^3): $[\bar{A}]_{1581} = 4.5 \times 10^2$; $[\bar{A}]_{1596} = 17.5 \times 10^2$; $[\bar{A}]_{1618} = 19.9 \times 10^2$.

It can be seen that: (1) All extinction coefficients decrease on passing from a higher area preparation to a lower area one; (2) all 8a modes of coordinated species have roughly the same extinction coefficients with a moderate dependence on the frequency; (3) the 8b mode possesses a definitely lower extinction coefficient than the 8a modes.

Tables 4 and 5 summarize the amounts of Py chemisorbed on the two preparations, when fully dehydrated. From the data in these tables, relative to the activation temperature for which the maximum total Py uptake is achieved on both preparations, we can deduce that:

(1) In the presence of a high Py pressure the coverage (i.e., the fraction of cus cations directly involved) in some 17 to 20% on both preparations. This suggests that the charge release from Py to the acidic center perturbs so much the insulator and must involve so many ions around the coordinating one that the screening effect produced upon coordination vacancy saturation is readily balanced.

(2) If we assume that Py chemisorption occurs at all of the defective Al centers, we deduce that the defective nature of the two preparations is quite limited, ~1 Al^{IV}/nm^2 existing on α-12 and ~0.5 on α-22.

(3) We do not know whether the defective centers are randomly distributed over the surface or concentrated in small areas.

TABLE 4

Chemisorbed Amounts (Py Molecules per nm^2) of the Various Species on a Fully Dehydrated α-12 Sample at Various Coverages

	P_{Py} = 8 Torr	After Py evacuation at 25°C	After Py evacuation at 100°C	After Py evacuation at 200°C
n_{1596} (Py_2)	0.72	0.43	0.15	0
n_{1616} (Py_3)	0.55	0.42	0.29	0.02
n_{1623} (Py_4)	0.30	0.30	0.26	0.16
n_{tot}	1.57	1.15	0.70	0.18
$R = n_{Py_2}/(n_{Py_3} + n_{Py_4})$	0.85	0.60	0.27	0

TABLE 5

Chemisorbed Amounts (Py Molecules per nm^2) of the Various Species on a Fully Dehydrated α-22 Sample at Various Coverages

	P_{Py} = 8 Torr	After Py evacuation at 25°C	After Py evacuation at 100°C
n_{1596} (Py_2)	0.95	0.65	0.05
n_{1618} (Py_3)	0.48	0.48	0.15
n_{tot}	1.43	1.13	0.20
$R = n_{Py_2}/n_{Py_3}$	1.98	1.35	0.33

In either case a close connection between these sites and the regular octahedral network is evidenced by the remarkable frequency shift produced on the Py/Al^{IV} bands by desorption of the Py/Al^{VI} species (see Figs. 1, 2, and 6).

(4) The last lines of Tables 4 and 5 report the ratios between Py molecules adsorbed at Al^{VI} and at Al^{IV}: The trend qualitatively evaluated on the basis of the ir intensities alone is confirmed and allows us to expect a regular crystal of α-Al_2O_3 to exhibit only the Py_2 species.

(5) Py uptake at Al^{VI} centers is very low (see the first lines of Tables 4 and 5), confirming the low acidity of these centers already indicated by CO (*1*) and CO_2 (*2*) adsorption. This may mean that only highly uncoordinated octahedral cations can chemisorb Py. In this respect we recall that Stone and Vickerman (*11*) have shown that a regular dehydration of the (0001) face of α-Al_2O_3 leaves 50% of the doubly uncoordinated Al^{VI} ions. It is also possible that the lower field of Al^{VI} ions, compared to Al^{IV}, causes the charge released by Py chemisorption to be shared by so many surrounding ions that the coverage is kept very low. We favor this idea, as it seems more consistent with the strong cooperative effects revealed by the adsorption–desorption of both Py and CO_2 (*3*).

(6) A comparison of the gravimetric data of Table 3 with the n_{tot} values of Tables 4 and 5 shows that the agreement is satisfactory. We think that, among the various sources of uncertainty, the major error lies in the assumption that all coordinated Py species possess the same extinction coefficient at 1580 cm^{-1} (mode 8b).

As far as the coverages on partly hydrated samples are concerned, the evaluated extinction coefficients can yield the concentrations of all species, giving a more quantitative meaning to the plots of Figs. 4 and 7. Only in the case of Py_2 can we not know how much of the total intensity at 1596 cm^{-1} is due to H-bonded Py and how much to Al^{VI}-coordinated Py. For example, after α-12 dehydration at ambient temperature and evacuation of Py at ambient temperature, Fig. 4 shows that we have: $\bar{A}_{1580} = 0.58$; $\bar{A}_{1596} = 1.3$; $\bar{A}_{1616} = 1.25$. On using the above reported coefficients we obtain: $n_{1580} = 0.42$ (per nm^2); $n_{1596} = 0.24$; and $n_{1616} = 0.21$. These figures indicate that:

(1) The number of molecules responsible for the absorbance of mode 8b corresponds reasonably well to the sum of all coordinated species, even on samples treated at temperatures different from that for which the extinction coefficients have been calculated.

(2) After a simple dehydration at room temperature, 0.21 Al^{IV} sites of the weaker type exist at the surface, i.e., one-half of the amount which can be revealed under the same conditions on a fully dehydrated sample.

(3) Only ~0.2 Py_2 molecules are at the surface (they will become at most 0.35 on the sample dehydrated at 100°C) and, in view of the very high hydration degree, this confirms that the Py/OH interaction through H-bonding is also quite scarce.

CONCLUSIONS

Py chemisorbs on variously dehydrated α-Al_2O_3 in small amounts, the coverage never exceeding 20% of the total surface. Nevertheless, the chemisorption process is a very heterogeneous one, several species being formed, corresponding to different field strengths. In particular there are very weak, weak, and strong fields. What is termed a very weak adsorption (Py_1) may either correspond to a simple nonspecific physical adsorption or to an extremely weak specific coordination, such that the splitting of modes 8a and 8b does not exceed the figure observed in the liquid phase.

Weak fields of comparable strength, as revealed by the same spectral features, are produced by a few surface OH groups available for N lone pair H-bonding and by some Al^{VI} ions. Strong fields for Py chemisorption are produced by some Al^{IV} ions, probably coming from a noncomplete surface transformation of Al^{IV} into Al^{VI}. These strong sites are themselves heterogeneous on short-treated preparations (Py_3 and Py_4 of α-12), while they become much less abundant and more homogeneous on longer-treated specimens.

The behavior of the $Py/\alpha\text{-}Al_2O_3$ system allows us to distinguish octahedral and tetrahedral Lewis acid sites and is thus bound to help a detailed assignment of the various Py species chemisorbed at the surface of transition aluminas, for which only an "inner and outer complex" definition (*5*) has been so far proposed. Finally, the low Py coverages and the variable spectral features of all bands with coverage and sample activation conditions confirm that, at the surface of an insulating oxide, chemisorption occurs through the creation of a specific local interaction and of lateral cooperative effects, so that the charge released to the surface (or withdrawn from the surface) is shared by a fair number of neighboring centers. An example of these lateral effects is given by the perturbation produced by coordinated Py molecules on adjoining surface OH groups through a π-cloud H-bonding.

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