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# 2,6-Disubstituted Pyridines as Probe Molecules for Surface Acid Sites—An Infrared Spectroscopic Study

It is well known that pyridine forms strong coordination bonds towards incompletely coordinated cations on alumina and other oxide surfaces (*1*). The formation of these coordinative chemisorption bonds is sterically hindered if the pyridine contains methyl groups in the 2- and 6-positions (*2*). Thus, Benesi (*3*) has suggested 2,6-dimethyl pyridine (26-DMP) as a proton specific probe. We have, however, demonstrated (*2*) that 2,4,6-trimethyl pyridine (246-TMP) still forms coordination bonds on alumina, although it is quantitatively displaced by the much weaker base pyridine: this is due to its coordination bond being more labile because of the steric interactions of the methyl groups with the surface. Very recently, Dewing *et al.* (*4*) have reported an infrared study of the adsorption of 2,6-di-*tert*-butyl pyridine (26-DTBP) on alumina. These authors claim to have detected acidic protons by the infrared bands of protonated 26-DTBP and a new type of Lewis acid site described as an electron-deficient oxygen species to which 26-DTBP can coordinate. They also present data which seem to indicate a displacement of pyridine by 26-DTBP. In this contribution we wish to present some infrared observations regarding the adsorption of 26-DTBP on a $\gamma$-$Al_2O_3$ sample (Degussa type P 110 C 1), which deviate from those reported by Dewing *et al.* We also give a different interpretation of the results based on alternative band assignments.

Apparatus and procedures were the same as previously described (*2*). Figure 1 shows a series of spectra obtained on adsorption of 26-DTBP in the temperature range between cell temperature (approximately 350 K) and 523 K on a $\gamma$-$Al_2O_3$ sample which was dehydroxylated at 923 K *in vacuo* ($<10^{-2}$ $Nm^{-2}$). In the presence of 26-DTBP vapor in the cell the characteristic bands of liquid 26-DTBP are observed. Two additional bands appear at 1618 and 1275 $cm^{-1}$. The surface OH groups which absorb at 3800 and 3740 $cm^{-1}$ are perturbed and a broader band centered at 3650 $cm^{-1}$ is produced, which shifts towards lower wavenumbers by 90 and 150 $cm^{-1}$ relative to the 3740 and 3800 $cm^{-1}$ bands, respectively. On adsorption of 26-DTBP on silica surfaces a displacement of the silanol stretching band by 100 $cm^{-1}$ towards lower wavenumbers occurs (*5*). This value compares very well with the corresponding shift of the O–H band on alumina in the present study. Similar shifts of the O–H band are also observed in the presence of adsorbed aromatic hydrocarbons (*6*). Therefore, it seems likely that the weakly adsorbed 26-DTBP interacts via $O\text{–}H\cdots\pi$ bonds with the surface hydroxyls on alumina. An $O\text{–}H\cdots N$ interaction apparently does not occur. We therefore believe that a protonation of 26-DTBP on an alumina surface is hardly probable. This agrees with the observation that neither 26-DMP (*4*) nor 246-TMP (*2*), both of which are stronger bases than 26-DTBP, are protonated on alumina.

On desorption at cell temperature, all bands of weakly adsorbed 26-DTBP are removed and the OH stretching bands are restored nearly to their original intensity except for the band at 3800 $cm^{-1}$. The re-

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maining bands are summarized in Table 1. The bands reported by Dewing *et al.* (*4*) in the 1400–1700 cm$^{-1}$ range also appear in our spectra with the same relative intensities; we observe, however, some more spectral details. The irreversibly held 26-DTBP shows an additional feature at 1275 cm$^{-1}$ and the $CH_3$ stretching and symmetric deformation vibrations are displaced by 10–20 cm$^{-1}$ towards higher wavenumbers as compared to the liquid. It can furthermore be seen from Fig. 1 that the intensity of the $CH_3$ stretching and symmetric $CH_3$ deformation (1370 cm$^{-1}$) vibrations remain practically constant on increasing the desorption temperature up to 523 K, while the intensity of the band near 1628 cm$^{-1}$ increases. The band at 1275 cm$^{-1}$ follows the trends of the band at 1628 cm$^{-1}$, although less pronounced.

These observations indicate that, while the number of chemisorbed species remains unaltered, the chemisorption bond character changes, thereby influencing the extinction coefficients of certain bands of the species. These bands certainly do not arise from 26-DTBP coordinated to incompletely coordinated $Al^{3+}$ ions. The Raman spectra of triethylaluminum complexes, for example, clearly show that, while coordination compounds are formed with 2,6-dimethyl substituted pyridines, 2,6-di-*tert*-butyl substitution prevents such complex formation (*7*). The bands ob-

TABLE 1

Infrared Absorption Bands (cm$^{-1}$)[a] for 26-DTBP Adsorbed on Alumina and in the Liquid State and for Substituted Pyridine-*N*-Oxides

| 26-DTBP | | | | *N*-Oxides[b] |
|---|---|---|---|---|
| Reversibly adsorbed | Irreversibly adsorbed | Pyridine preadsorbed | Liquid | |
| 3080 (ms) | 3095 (w) | | 3080 (ms) | |
| | | | 3060 (w) | |
| 2960 (vs) | 2977 (vs) | 2960 (vs) | 2958 (vs) | |
| 2903 (ms) | 2918 (ms) | 2903 (ms) | 2903 (ms) | |
| 2865 (ms) | 2880 (ms) | 2868 (ms) | 2865 (ms) | |
| | 1620–1628 (vs) | | | 1600–1645 |
| | | | 1587 (ms) | |
| 1574 (vs) | 1573 (w) | 1577 (vs) | 1577 (vs) | |
| | 1547 (w) | | | 1535–1580 |
| | 1505 (ms) | | | |
| 1480 (s) | 1482 (vw) | 1480 (ms) | 1480 (s) | 1480–1486 |
| 1450 (s) | 1455 (w) | | 1452 (s) | |
| | 1430–1435 (ms) | | | 1434–1443 |
| 1403 (ms) | 1400 (w) | | 1407 (ms) | |
| 1389 (ms) | | | 1389 (ms) | |
| 1359 (s) | 1370 (ms) | 1360 (ms) | 1359 (s) | |
| 1272 (w) | 1275 (w) | | 1274 (w) | 1220–1300 ($\nu$ $N^+$–$O^-$) |
| 1242 (ms) | | | 1246 (ms) | |
| 1223 (w) | | | 1227 (w) | |
| 1199 (w) | | | 1203 (w) | |
| 1160 (w) | | | 1163 (ms) | 1150–1169 |
| 1144 (ms) | | | 1148 (s) | |
| 1096 (w) | | | 1099 (ms) | 1080–1120 |

[a] Band intensities: vs, very strong; s, strong; ms, medium strong; w, weak; vw, very weak.

[b] Refs. (*8*) and (*9*).

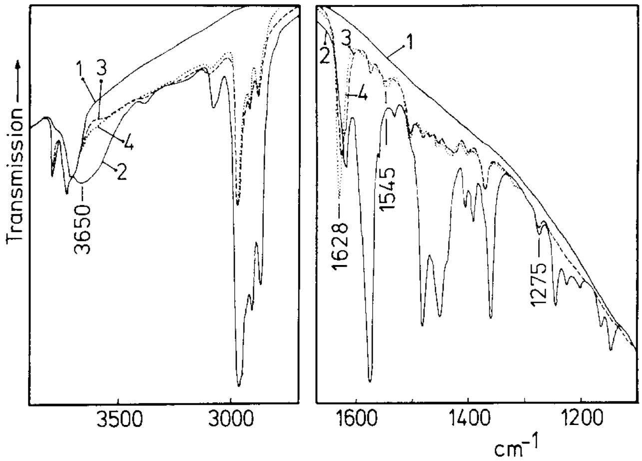

FIG. 1. Infrared spectra of 26-DTBP adsorbed on $\gamma$-$Al_2O_3$ pretreated at 923 K: (1) background; (2) adsorption at cell temperature at saturation vapor pressure; (3) after desorption at 373 K; (4) after desorption at 523 K.

served for chemisorbed 26-DTBP are compared with those of the liquid and of pyridine-*N*-oxides in Table 1. The fairly good correspondence of the sets of bands of the chemisorbed species and of pyridine-*N*-oxides lends some support to the suggestion that 26-DTBP forms a chemisorption species on extremely exposed oxygen species [possibly similar to those suggested by Dewing *et al.* (*4*) as electron deficient oxygen species], over which the 26-DTBP can be draped, the $N^+$–$O^-$ bond being more fully developed as the adsorption temperature increases. This reaction is certainly sterically hindered, but the strong inductive effect of the *tert*-butyl groups facilitates the attack of the oxygen species. This, and the fact that there is no competition by Lewis acid sites for the 26-DTBP, explains the complete absence of analogous surface species of pyridine or methyl pyridines. We thus reject the band assign-

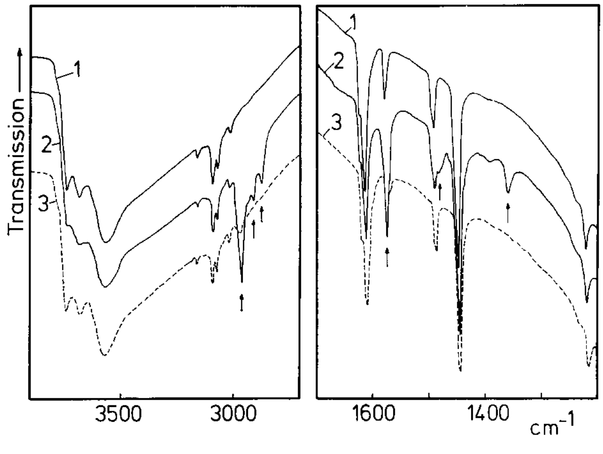

FIG. 2. Infrared spectra of pyridine and 26-DTBP on $\gamma$-$Al_2O_3$ (pretreated at 773 K): (1) pyridine adsorbed and desorbed at cell temperature; (2) 26-DTBP on 1 at cell temperature; (3) after desorption of 26-DTBP at cell temperature (characteristic 26-DTBP bands indicated by arrows).

ments given by Dewing *et al.* and we believe that none of the observed bands—including the one at 1545 $cm^{-1}$—can be attributed to a protonated 26-DTBP species. This conclusion is in agreement with the observed perturbations in the OH stretching region mentioned above.

The exposed oxygen species must obviously be surrounded by exceptionally strong Lewis acid sites (incompletely coordinated $Al^{3+}$ cations), which should retain pyridine preferentially. As shown in Fig. 2, the modification of the alumina surface by pyridine adsorption and desorption at cell temperature completely suppresses the oxidation of 26-DTBP and allows only for the weakly adsorbed species which is readily removed on pumping. The intensity of the characteristic pyridine bands decreases only slightly due to the increased evacuation time, whereas a displacement of pyridine by 26-DTBP as reported by Dewing *et al.* (*4*) cannot be observed. On the contrary, presorbed pyridine makes the exposed oxygen species inaccessible for 26-DTBP.

It should finally be mentioned that a completely static surface model most probably cannot account for all the experimental observations. It is this point which leads Dewing *et al.* (*4*) to reject the possibility of coordinative interactions with incompletely coordinated cations even for 26-DMP. Most probably, however, the surface ions of an oxide surface, particularly a strongly disordered surface, will not remain in absolutely fixed positions, but at least local surface reorganizations may occur under the action of temperature and adsorbate. Thus, bonding to an incompletely coordinated $Al^{3+}$ ion may be facilitated by a displacement from its coordination site towards the surface. Analogous arguments have been put forward by Kokes and Dent (*10*) to explain the bonding of $\pi$-allyl species on Zn sites on the surface of zinc oxide. It is our feeling that the chemisorption behavior of 2,6-dimethyl-substituted pyridines can in fact be interpreted on the grounds of the classical picture of a Lewis acid site and that a modification as suggested by Dewing *et al.* is not necessary.

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