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LETTERS TO THE EDITORS

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

In a recent Note with the above title, Knözinger, Krietenbrink and Ratnasamy (*1*) reported results which show some similarities and some differences to those presented in our earlier paper (*2*) on the adsorption of hindered pyridines on alumina.

The similarities are first, the observation of very similar spectra for adsorbed 2,6-ditertiarybutylpyridine (2,6T) and secondly, that this base is strongly adsorbed on γ-alumina. Knözinger *et al.* (*1*) concluded that the site for adsorption of this hindered pyridine may be a surface oxygen species similar to that postulated by ourselves. The differences, however, are significant. Knözinger *et al.* have failed to observe the displacement of preadsorbed pyridine by 2,6T and have questioned our assignment of the band at 1545 cm^{-1} to a protonated 2,6T species.

With regard to the displacement by 2,6T, our results were obtained reproducibly in the series of experiments. We restate our confidence in them. The assignment of bands to specific species in our paper relied on the interpretation of relative band intensities seen in a series of competitive adsorption experiments. Quantitative analysis of the data led us to conclude that there was evidence for four different acid sites, one of which was a protonic acid. The values quoted in Table 2 of our paper show clearly that the relative intensity of the 1545 cm^{-1} band varies significantly when compared with the bands at 1508 and 1430 cm^{-1}, indicating that it fingerprints the presence of at least two different types of adsorbed 2,6T. The assignment of this band to a protonated species was made on the basis of the observation of a 1535 cm^{-1} band in spectra of both 2,6T hydrochloride and 2,6T adsorbed on silica–alumina that had been previously treated with pyridine. In this latter experiment the displacement of the pyridinium ion and the formation of the new species was clearly observed. The fact that on alumina this band is shifted to 1545 cm^{-1} and that the species is retained on heating *in vacuo* to 250°C indicates that this site involves more than just protonation by a weak acid site.

The differences in the experimental results may arise from the different thermal pretreatments (650°C in the work of Knözinger *et al.* rather than 350°C in our work) or perhaps more importantly, a different alumina. We have observed, for instance, in pyridine adsorption significant differences in the relative intensities of the bands at 1455 and 1230 cm^{-1} on Ketjen aluminas 0003P and CK300, both shown by XRD to be γ-alumina. We further note that the pattern of –OH bands shown by Knözinger *et al.* is significantly different from that of both the Ketjen aluminas we studied.

Assignment of the bands below 1300 cm^{-1} is important in understanding the possible role of oxygen as an adsorption site for pyridine bases. We too had noted the similarities of some spectral features of pyridine N-oxides, their complexes (*3*) and pyridine adsorbed on alumina. In an at-

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tempt to resolve the uncertainty about band assignments we have recorded the spectrum of ^{15}N-pyridine adsorbed on alumina. ^{14}N-Pyridine shows a doublet at 1245 and 1230 cm^{-1} while ^{15}N-pyridine shows only a single band at 1230 cm^{-1}, of increased intensity relative to the 1455 cm^{-1} band. This indicates a shift of the 1245 cm^{-1} by 15 cm^{-1} to lower frequency on substitution of ^{14}N by ^{15}N. This result is consistent with the band being due to N–O bonding. This work will be reported in more detail at a later date.

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