

Letter to the Editor

An example of misinterpretation of IR spectra of adsorbed species due to gas phase H₂O: Comment on “The surface acidity and characterization of Fe-montmorillonite probed by in situ FT-IR spectroscopy of adsorbed pyridine” [Appl. Catal. A 294 (2005) 156–160]

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Catalytic activities of metal oxides are governed by their surface properties. Infrared spectroscopy of adsorbed probe molecules is one of the most powerful techniques allowing the characterization of acid–base properties of high surface area metal oxides. Among the probe molecules routinely used, pyridine is certainly the most employed: thousands papers – more than one hundred each year – have reported surface characterization using IR spectroscopy of pyridine adsorbed on all kinds of materials. As a strong base, pyridine easily forms H-bonded (HPy) and pyridinium (BPy) species with weak and strong Brønsted acid sites, respectively, as well as coordinated species (LPy) on Lewis acid sites. These various species are easily identified and distinguished by examination of the 1700–1400 cm^{−1} range (8a, 8b, 19a and 19b ring stretching vibrations).

In a recent article [1], this method has been employed to characterize surface acidity of Fe-montmorillonite. For the sake of clarity, the experimental IR spectra presented in this article are reproduced in Fig. 1A. The author has reported more than 20 sharp bands (FWHH ~ 2–3 cm^{−1}) in the 1700–1400 cm^{−1} range, which he has assigned to coordinated (LPy), H-bonded (HPy) and protonated (BPy) pyridine species (Table 1 in ref. [1]). It is well known that actual IR spectra of HPy, BPy and LPy species are strongly different. In Fig. 2, we have reported the IR spectra of liquid pyridine and pyridine adsorbed on silica (HPy), H–Y zeolite (BPy) and ZrO₂ (LPy). It clearly appears that all these bands are much broader (FWHH ~ 7–12 cm^{−1}) than those reported in ref. [1]. Moreover, whatever the species formed upon adsorption, no band is observed above 1640 cm^{−1} as well as in the 1500–1530 cm^{−1} or in the 1460–1480 cm^{−1} ranges, whereas the author has assigned some bands in these regions to pyridine species. Thus, most of the bands reported in ref. [1] are not due to adsorbed pyridine. Anyone having a basic practice of IR spectroscopy should recognize that such bands are due to atmospheric water along the beam path, inside the spectrometer. This is clearly demonstrated by Fig. 1B that

shows a spectrum of gas phase water recorded at the resolution used in ref. [1] (2 cm^{−1}). The intensity of gas phase H₂O bands in Fig. 1A is so large that all bands due to pyridine are masked, except for spectra (b and c), where pyridine bands can be observed at 1595, 1490 and 1443 cm^{−1} (ν_{8b}, ν_{19a} and ν_{19b}, respectively). These wavenumbers are close to those observed for H-bonded (HPy) or weakly coordinated (LPy) species and, as noticed by the author, do not indicate that strong adsorption sites are detected by pyridine. On the other hand, a very strong and broad band at ~1635 cm^{−1}, not noticed by the author, appears in spectrum (b) and grows in spectra (c–d). This broad band is probably due to the δ(HOH) mode of adsorbed H₂O. This indicates either that pyridine was not dried before use or that water readsorbed from the walls of the IR cell, or that the IR cell was leaking during the experiment. In any case, the

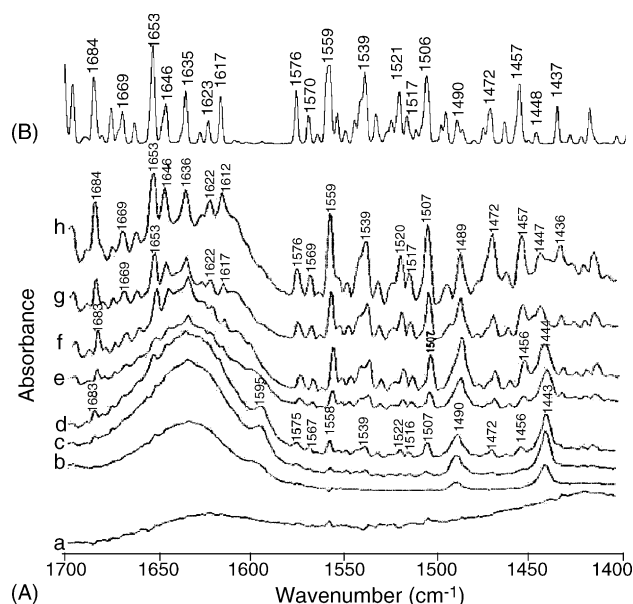


Fig. 1. (A) IR spectra of ref. [1] and (B) IR spectrum of atmospheric water (Magna 550 Nicolet Spectrometer, 2 cm^{−1} resolution).

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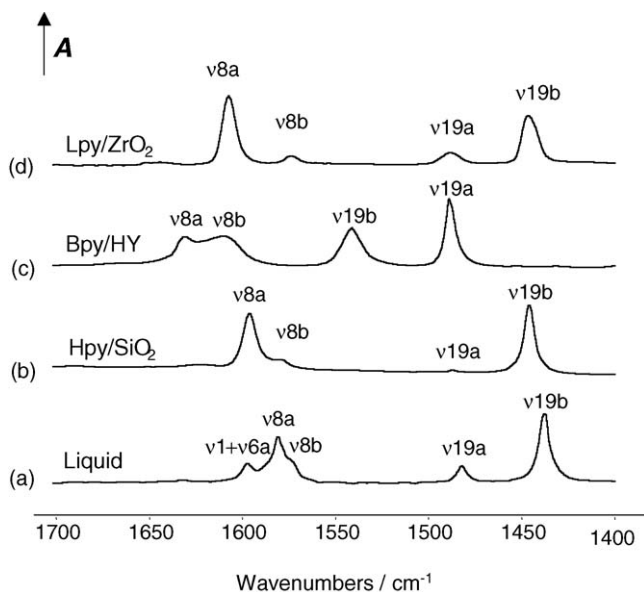


Fig. 2. IR spectra of (a) liquid pyridine and pyridine adsorbed on (b) SiO_2 , (c) H-Y zeolite and (d) ZrO_2 .

occurrence of this band suggests that strong adsorption sites, if any, are probably poisoned by adsorbed water.

Finally, most of the bands reported in this paper, and particularly all those used to assess Brønsted and Lewis acidity of Fe-montmorillonite (Tables 1 and 2; Fig. 2 in ref. [1]) are due to atmospheric water. Also, the requirement of an activated

surface (without adsorbed water) before pyridine adsorption was not met. We have to conclude that nothing of value can be derived from this study because of beginner mistakes. Publication of such a paper discredits the work of all IR spectroscopists in the field of heterogeneous catalysis. We are really disappointed to have to make such a comment, more than 40 years after the work of Parry: “An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity” [2].

References

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