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Pyridine adsorption reveals high-coordinated cationic centres at the surface of microcrystalline ZnO

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The adsorption of pyridine at 300 K on microcrystalline ZnO has been investigated by FTIR spectroscopy. Besides an interaction by H-bonding with surface OH groups, evidence is found for the Lewis coordination of pyridine onto coordinatively unsaturated surface Zn^{2+} centres possessing a regular tetrahedral coordination, as well as onto some other surface Zn^{2+} centres, only slightly uncoordinated. The creation at the surface of the ZnO of cationic centres with an anomalous coordination higher than 4 (quasi-octahedral) is thus postulated. No such high-coordinated Zn^{2+} centres seem to form to an appreciable extent when ZnO is dispersed (at least at up to a 3% weight level) at the surface of other microcrystalline oxides such as, for instance, TiO_2.

Keywords: Zinc oxide; ZnO microcrystals; IR spectroscopy; pyridine adsorption; surface Lewis acidity; surface reconstruction

1. Introduction

Since Parry first investigated the behaviour of pyridine (py) as an adsorbate by IR spectroscopy [1], the use of this probe molecule has become very common, and turned out to be particularly useful in revealing the possible simultaneous/competitive presence of Lewis and Brønsted acidity at the surface of various oxidic systems.

Using the coordination of py onto Lewis acidic centres (this species will be hereafter referred to as [py-L]), the spectral analysis in the mid-IR region of the 8a–8b and 19a–19b "ring" modes of py [2] has been mostly adopted to reveal the presence and the nature of strong surface acidic centres. The latter are surface cationic sites carrying a strong coordinative unsaturation (cus surface cations), at which adsorbed [py-L] species exhibit 8a and 19b modes at frequencies higher than in the free py molecule, and onto which [py-L] species remain adsorbed after evacuation at temperatures as high as ≈ 473 K (e.g., see [3–5]).

More recently, the use of a strong Lewis base such as py has also been proposed as a suitable tool also to reveal weak surface Lewis acidic centres [6]. The latter are slightly un-coordinated surface cationic centres, towards which other probe molecules such as CO or CO_2, sensitive to strong acidic centres, are largely insensitive, being too weakly basic.

Revealing weak surface acidic sites requires the study of the IR spectroscopic features of adsorbed py before the thermal desorption and, possibly, even before simply evacuating the py at ambient temperature. In these conditions, all chemisorbed py species are present with their maximum intensity (top coverage), and are still in the presence of a physically adsorbed py phase ([py-ph]). The utility of this approach, and the procedures of band-subtraction and band simulation needed for it, have been reported elsewhere [6].

It has been possible to reveal the formation of weak and partly reversible [py-L] species chemisorbed onto weak acidic sites, for instance cus octahedrally coordinated Al^{3+} centres [7,8] or cus alkali metal ions [9], which otherwise would easily escape detection.

The aim of the present contribution is to show that, at the surface of microcrystalline ZnO, there are some weak acidic sites, that py adsorption at 300 K is able to reveal.

2. Experimental

MATERIALS

Two zinc oxide based materials have been used: (i) Pure *ZnO* (Kadox 25, New Yersey Zinc Co.). This material has a BET surface area of 9–12 $m^2\ g^{-1}$, and has been shown by Scarano et al. [10] to present a fairly regular crystallographic habit, in which the (1010) prismatic termination is by far predominant. Samples of ZnO are designated in the text and figures by the symbol Z, followed by a numerical indicating the temperature (K) at which the samples were vacuum activated and oxidized before adsorbing py at 300 K. (ii) *ZnO/TiO*$_2$ (1% weight Zn), deriving from the oven decomposition at 673 K of Zn acetate dispersed by impregnation at incipient wetness on TiO_2 (anatase P25, by Degussa). After decomposition, the material was (re)hydrated by long exposure to the atmosphere. The P25 support has a BET surface area of 48 $m^2\ g^{-1}$, and has been shown by Spoto et al. [11] to possess a regular crystallographic habit, in which the termination along the (010) crystal plane is predominant. Electron micrographs indicate that this termination is not appreciably modified by the impregnation with Zn acetate and subsequent decomposition. ZnO/TiO_2 samples are designated in the text and figures by the symbol ZT, followed by a numeral indicating the temperature (K) at which the samples were vacuum activated and oxidized before adsorbing py at 300 K.

IR SPECTRA

IR spectra have been run, with a strictly in situ configuration so the results are semi-quantitative, at 4 cm^{-1} resolution on a Bruker 113v FTIR spectrophotometer, equipped with an MCT detector. Spectral subtractions and band simulations have been carried out, on non smoothed spectra, using standard programs by Bruker.

All samples were prepared for IR measurements in the form of thin layer depositions (4–10 mg cm^{-2}) over a pure Si platelet.

3. Results and discussion

Fig 1 shows, in the spectral range of the 8a–8b modes (section A) and of the 19b mode (section B), the spectra of py adsorbed on various Z samples. Curves a–b of sect. IA show that, under *a* ≈ 10 Torr py pressure (i.e., at high py coverage), there are at least three py chemisorbed species, characterized by a common 8b mode at ≈ 1575 cm^{-1} and different 8a modes, centered at ≈ 1612 cm^{-1} (species P_1), ≈ 1594 cm^{-1} (species P_2), and ≈ 1589 cm^{-1} (species P_3) respectively.

Upon very short py evacuation at ambient temperature (curves c–d of sect. IA), the P_3 species is abundantly desorbed, the P_2 species declines, whereas the P_1 species does not desorb at all. They thus reveal rather different stabilities, which are consistent with the differing upwards shift of the relevant 8a modes relative to the free py molecule.

The 19b region (sect. IB) exhibits a similar complexity, although the P_2 and P_3 components (≈ 1445 and ≈ 1440 cm^{-1} respectively) are less resolved than they are in the 8a region.

Upon increasing the activation/oxidation temperature, the Z samples achieve a higher surface dehydration, and the three chemisorbed py species vary, following a different trend. This is shown by the spectra of sets II and III of fig. 1: the P_1 species increases steadily and abundantly, the P_2 species remains fairly constant, and the P_3 species declines sharply. Note that the varied relative intensities permit the observation of the presence of three py species both in the 8a and in the 19b mode range. This is more clearly shown by the resolved curves d.

The behaviour of the P_1 species is indicative of a strong [py-L] coordinative interaction (confirmed by the complete non reversibility upon evacuation), occurring at strong cus surface cationic sites, whose population increases following the surface dehydroxylation.

The behaviour of the P_3 species is indicative of a weak H-bonding interaction ([py-H]), occurring at surface OH groups, whose population declines sharply with vacuum thermal treatment.

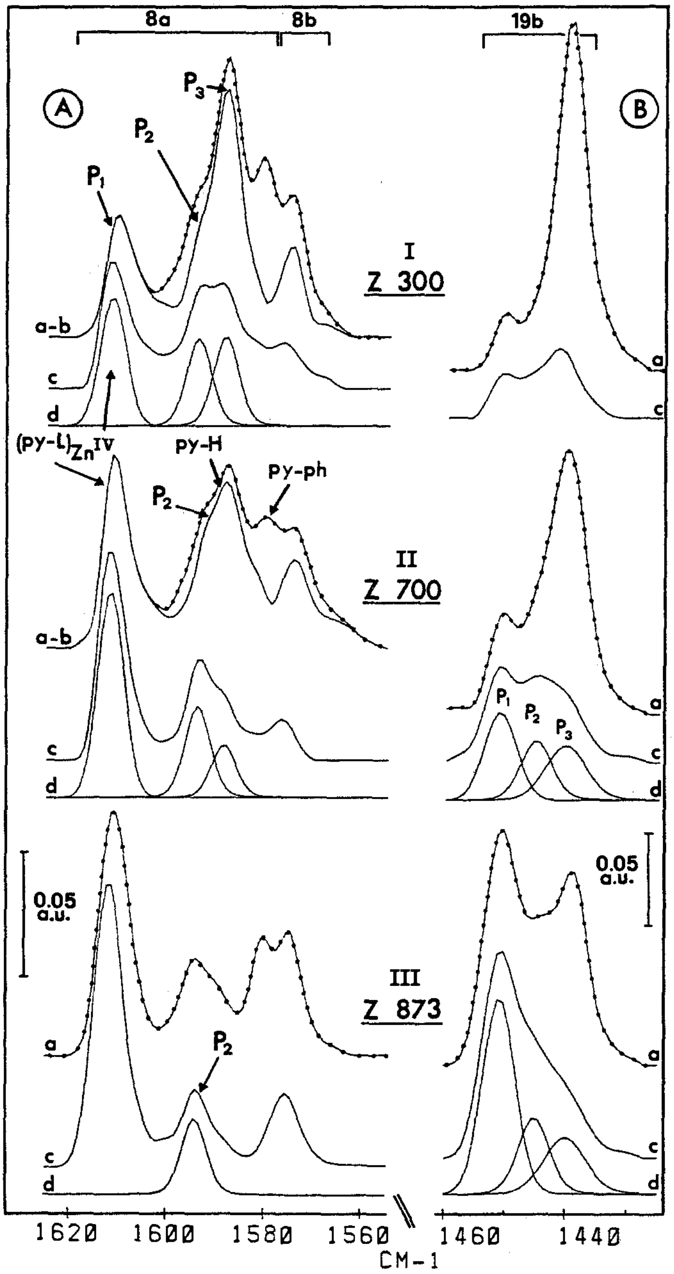

Fig. 1. Segments of the IR spectra of py adsorbed at 300 K on ZnO activated/oxidized at (K): 300 (I), 700 (II), 873 (III). *Curves a (dotted line): ≈ 10 Torr py adsorbed. Curves b*: as curves a, after band subtraction of the spectral contribution of the physically adsorbed [py-ph] phase. *Curves c*: after 2 min py evacuation at 300 K. *Curves d*: some band-resolved components of the spectra of curves c.

For the P_2 species, the formation of a weaker [py-L] species, occurring at slightly uncoordinated surface cationic centres, is suggested by: (i) its behaviour upon desorption (P_2 desorbs in part at 300 K but, not shown in fig. 1, it desorbs entirely upon short evacuation at ≈ 400 K); (ii) the spectral position of its analytical "ring" modes (and, in particular, of the mode 8a); (iii) the low intensity and the virtually complete non dependence of its bands on surface dehydration. The population of these centres is probably small, and already virtually complete after simply evacuating at ambient temperature.

In the crystalline structure of ZnO (wurtzite-type), Zn^{2+} ions are known to occupy the tetrahedral cavities (Zn^{IV}), so that Zn^{IV} cations are also expected to be present at the surface, and especially in the case of an ordered and regular termination of the crystallites.

The spectral features of the strongly held P_1 species are all consistent with [py-L] coordination at cus Zn^{IV} centres. In fact cus tetrahedrally coordinated cations are known (for instance, in the case of transition aluminas) to be strong Lewis acidic sites, and to yield [py-L] species whose 8a and 19b modes absorb at above ≈ 1610 and ≈ 1450 cm^{-1} respectively [12].

The P_2 species should be thus ascribed to a [py-L] complex occurring at cus Zn^{2+} surface sites, whose coordination number is larger than 4 (e.g., pseudo-octahedral), and whose coordinative unsaturation is low and easily achieved in vacuo at low temperatures, for instance upon desorption of weakly coordinated undissociated water molecules. Incidentally, the spectral position of the 8a mode of the [py-L] P_2 species is very close to that of [py-L] complexes formed on cus Al^{VI} sites at the surface of aluminas [7,12].

This result is quite unexpected. In general, surface defects tend to exhibit lower (rather than higher) coordination compared to the corresponding bulk cations, although an increase in the coordination number of surface Zn^{2+} ions to greater than 4 has been postulated by other authors [13,14]. In particular, Tsyganenko et al. [14] suggested that "surface Zn atoms, due to their large ionic radius, may have a larger coordination number with respect to oxygen than in bulk ZnO". At high pressures, ZnO has been reported to form an NaCl-type lattice with six-fold coordinated Zn atoms [15].

Fig. 2 shows results from the ZnO/TiO_2 system. This shows in our opinion that the formation, at the surface of the Zn-containing oxide systems, of high-coordinated (and thus slightly uncoordinated) Zn^{2+} centres is not restricted to Zn itself, but is characteristic of the surface chemistry of (micro)crystalline ZnO.

Py uptake on ZT samples generates three main chemisorbed species: (i) a strongly held $[py\text{-}L]_{Zn}$ species (8a mode at ≈ 1610 cm^{-1} and 19b mode at ≈ 1450 cm^{-1}), ascribed to the coordination onto cus Zn^{IV} surface centres; (ii) a strongly held $[py\text{-}L]_{Ti}$ species, due to coordination onto cus surface Ti^{4+} sites (8a mode at ≈ 1604 cm^{-1} and 19b mode at ≈ 1445 cm^{-1}, as observed at the surface of pure TiO_2 [16]); (iii) a weakly held [py-H] species, due to H-bonding

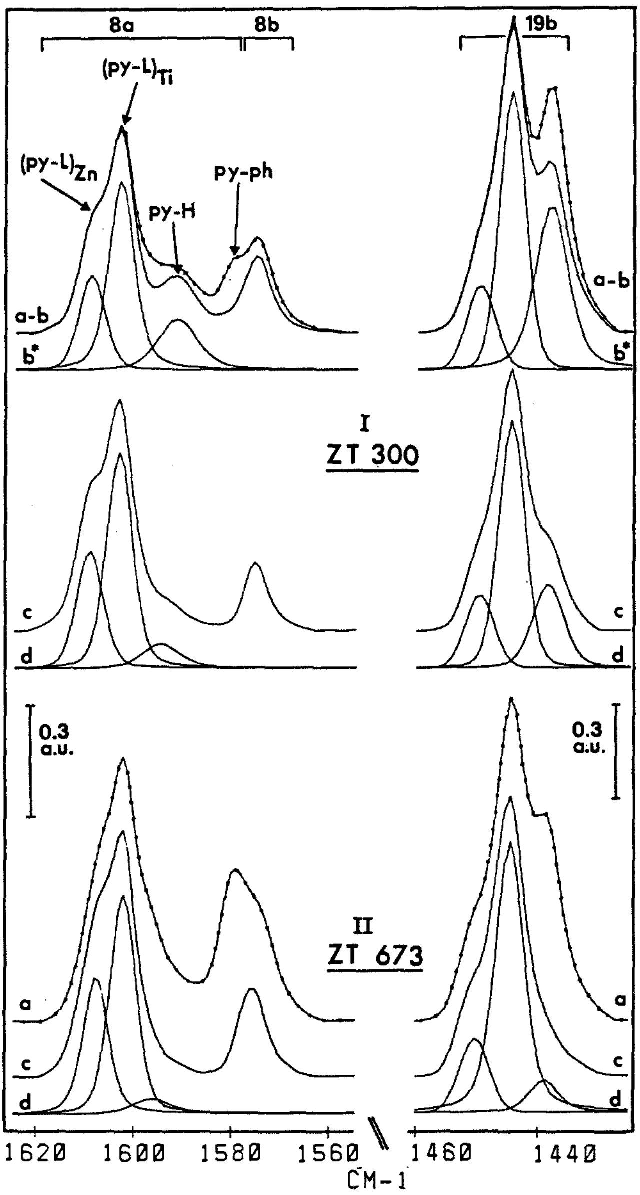

Fig. 2. Segments of the IR spectra of py adsorbed at 300 K on ZnO/TiO_2 activated/oxidized at (K): 300 (I), 673 (II). *Curves a* (*dotted line*): ≈ 10 Torr py adsorbed. *Curves b*: as curves a, after band subtraction of the spectral contribution of the physically adsorbed [py-ph] phase. *Curves b* *: some band-resolved components of the spectra of curves b. *Curves c*: after 2 min py evacuation at 300 K. *Curves d*: some band-resolved components of the spectra of curves c.

with surface OH groups (8a mode at ≈ 1594 cm^{-1} and 19b mode at ≈ 1438 cm^{-1}). The latter species is scarce, compared to ZnO (see fig. 1), and its amount decreases fast with evacuation (compare curves b and c of set I) and with dehydration (compare the corresponding bands b in set I and II of fig. 2). Within the resolved bands ascribed to the [py-H] species there is no evidence for the presence of any other component possibly assignable to a [py-L] species coordinated onto cus Zn^{2+} surface centres with a coordination higher than 4.

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