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Brønsted acidity in HY zeolites measured by IR study of pyridine adsorption: influence of steric effects

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The formation of pyridinium ions upon pyridine sorption on HY samples of varying Al composition has been studied by IR spectroscopy. It is demonstrated that HY supercages cannot accommodate more than four pyridinium ions. This property is shown to affect the ability of LF protons to migrate towards positions accessible to pyridine and form pyridinium ions. The mode of interaction of LF hydroxyls with pyridine is discussed in the light of both steric and electrostatic parameters.

Keywords: acidity; HY; zeolite; pyridine; IR spectroscopy

1. Introduction

Since the pioneering work by Basila et al. who studied the adsorption of pyridine on silica alumina by IR spectroscopy [1], pyridine has extensively been used to probe Brønsted and Lewis acidity in catalytic materials. Specific IR vibrations could be identified, depending on the type of interaction of the molecule with surface sites. As an example, the 19b vibration mode ascribed to combined C–C stretching and N–H bending modes was found at 1439 cm^{-1} for the gas phase, 1438 cm^{-1} for pyridine physically adsorbed on silica alumina, 1450 and 1545 cm^{-1} for pyridine chemically sorbed respectively on Lewis and Brønsted acid sites. When adsorbed in HY zeolite pores, pyridine was shown to form pyridinium ions (characterized by an intense band at 1540 cm^{-1}) [2] by interaction with the so-called HF hydroxyls, siting in the supercages and vibrating at 3640 cm^{-1}. The HY zeolite structure presents a second type of hydroxyls, the so-called LF hydroxyls, vibrating at 3550 cm^{-1} and located in sterically less accessible cavities (sodalite cages and hexagonal prisms) [3]. Although not accessible to pyridine because of too small a cage opening, LF sites have been shown to interact with pyridine, which suggested the mobility of interacting LF sites toward positions accessible to pyridine, i.e. supercages [4]. The nature of the bonding between pyridine and LF hydroxyls was recently clarified by Parker et al. [5]: a partial protonation of pyridine was suggested. We wish to report here the influence of steric effects on the quantitative evaluation of Brønsted acidity in HY zeolites by pyridine sorption. This is achieved by an IR investigation of pyridine adsorption on a series of HY zeolite samples of varying Al composition. The modes of interaction of pyridine with HF and LF hydroxyls are discussed in the light of pore filling effects.

2. Experimental

The parent NH_4Y sample (Si/Al = 2.5) was obtained by conventional exchange of NaY (Union Carbide) in aqueous NH_4Cl solution (pH = 6) at room temperature. A series of dealuminated samples was prepared using $SiCl_4$ as dealuminating agent according to a procedure already described [6]. Samples of varying Si/Al ratios, designated as HY-4.5, -4.8, -11.1 where the sample coding reflects the Si/Al ratio from chemical analysis, were obtained by changing the dealumination temperature between 473 and 673 K. Another dealuminated sample (HY-5.7) was prepared by reacting the NH_4Y sample at 353 K with $(NH_4)_2SiF_6$ solutions buffered with ammonium acetate [7]. We report in table 1 the main physicochemical characteristics of the solids.

From XRD results, it can be observed that all our

Table 1
Framework Al (Al_F) composition (measured from ^{29}Si NMR measurements), global Al composition (measured by atomic absorption analysis) and crystalline fraction (%C) of parent and dealuminated HY samples determined from XRD

Sample	a_0 (nm)	Al_F/u.c. ^{29}Si NMR	Al/u.c. CA	%C XRD
HY-2.5	2.472	55.3	52.7	100
HY-5.7	2.445	35.9	28.7	100
HY-4.5	2.445	24.9	34.9	98
HY-4.8	2.437	19.4	32.8	97
HY-11.1	2.427	4.5	15.9	104

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HY samples are highly crystalline (%C$\geqslant$97). ^{29}Si NMR results indicate that, depending on the type and severity of dealuminating treatment the framework Al composition has been extensively varied (between 4.5 and 55 aluminum atoms per unit cell). However, there exists some discrepancy between the atomic Al compositions of dealuminated samples given by NMR and chemical analysis, indicating the presence of extraframework Al species. In the case of the SiCl$_4$ series, the framework Al composition is less than the Al composition determined by chemical analysis, which indicates the presence of significant amounts of extraframework Al species. The reverse is observed for the sample dealuminated by (NH$_4$)$_2$SiF$_6$. This is ascribed to the presence of an extraframework amorphous Si-rich phase on the inner and/or outer zeolitic surface, resulting from the hydrolysis of SiF$_4$ entities [8].

For IR measurements, samples were pressed into self-supporting wafers, introduced into the IR cell, heated up to 623 K at 0.5 K min^{-1} in flowing O$_2$ and subsequently evacuated under vacuum for 4 h at 623 K. 10 Torr (1 Torr = (101325/760) Pa) of pyridine were admitted into the cell at room temperature before evacuation under vacuum at 423 K. IR spectra were recorded at room temperature with a Perkin Elmer 580 IR spectrometer at a resolution of 4 cm^{-1}.

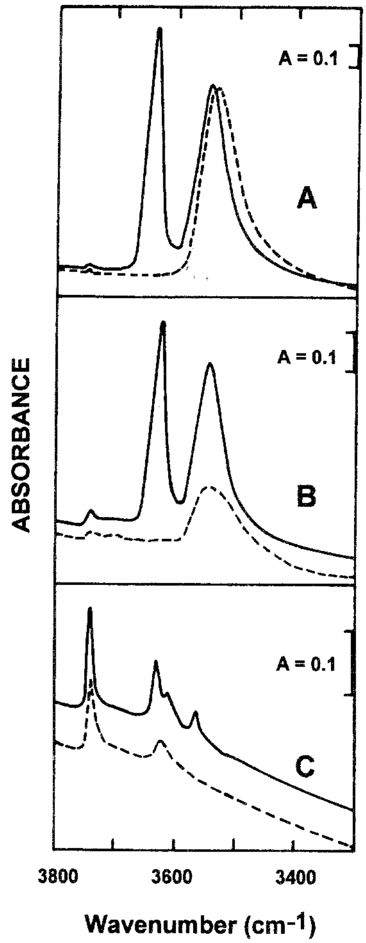

Fig. 1. νOH vibrations of HY samples containing (A) 56 Al/u.c., (B) 36 Al/u.c. and (C) 4.5 Al/u.c. after activation (solid line) and after pyridine sorption and subsequent evacuation at 423 K (dashed line).

3. Results and discussion

Fig. 1 shows the IR spectra, in the νOH region, of parent HY-2.5, HY-5.7 and HY-11.1 samples after activation (solid line) and after pyridine sorption and subsequent evacuation in vacuo at 423 K (dashed line). After activation, samples are all characterized by the doublet at about 3650 and 3550 cm^{-1} characteristic of HF and LF hydroxyls. It can be noticed that the intensity of these bands decreases with increasing dealumination extent. Upon dealumination, the 3650 cm^{-1} band is observed to shift towards lower wavenumbers while the LF νOH band is shifted upwards. The bathochromic shift of the νOH of the HF hydroxyls is consistent with an increase of the acid strength of the HF hydroxyls upon dealumination, as already evidenced by the use of probe molecules [9], ^{1}H MAS NMR [10] and theoretical calculations [11]. The hypochromic shift of the νOH of the LF hydroxyls is easily explained by a decrease, upon decreasing the Al content, of the electrostatic interactions with the surrounding oxygens (these interactions are thought to be responsible for the low LF frequency compared to that of the HF hydroxyls). For samples dealuminated by SiCl$_4$ (see fig. 1C), a 3740 cm^{-1} band appears due to SiOH groups and an additional broad νOH band at about 3600–3610 cm^{-1} is observed, ascribed to the hydroxyls of extraframework Al species. Because it is only partly affected upon pyridine sorption and totally regenerated upon pyridine desorption at 423 K, this band is ascribed to hydroxyls inaccessible to pyridine and weakly acidic.

The heights I_{HF} and I_{LF} of the νOH bands of the HF and LF hydroxyls respectively were measured for the samples where the 3600–3610 cm^{-1} band is absent or weakly intense, i.e. the HY-2.5, HY-5.7 and HY-4.5 samples. The values of the ratio $I_{\mathrm{HF}}/I_{\mathrm{LF}}$ obtained for the HY-2.5, HY-5.7 and HY-4.5 samples were 1.26, 1.19 and 1.06 respectively. This result suggests that, for samples containing more than 25 atoms per unit cell, the HF and LF hydroxyls populations vary in the same proportions upon dealumination.

After pyridine sorption and subsequent evacuation at 423 K (see fig. 1), HF hydroxyls of all samples are observed to totally interact with pyridine as shown by the total disappearance of the 3650 cm^{-1} band. *The striking feature is the strong dependence of the interaction of LF hydroxyls with pyridine when varying the framework Al composition*: while not affected by pyridine in the parent HY sample (fig. 1A), LF hydroxyls are more and more consumed upon pyridine sorption when decreasing the framework Al content (Figs. 1B and 1C). Simultaneously, the formation of pyridinium ions (PyH$^+$) was observed, characterized by a band at 1540

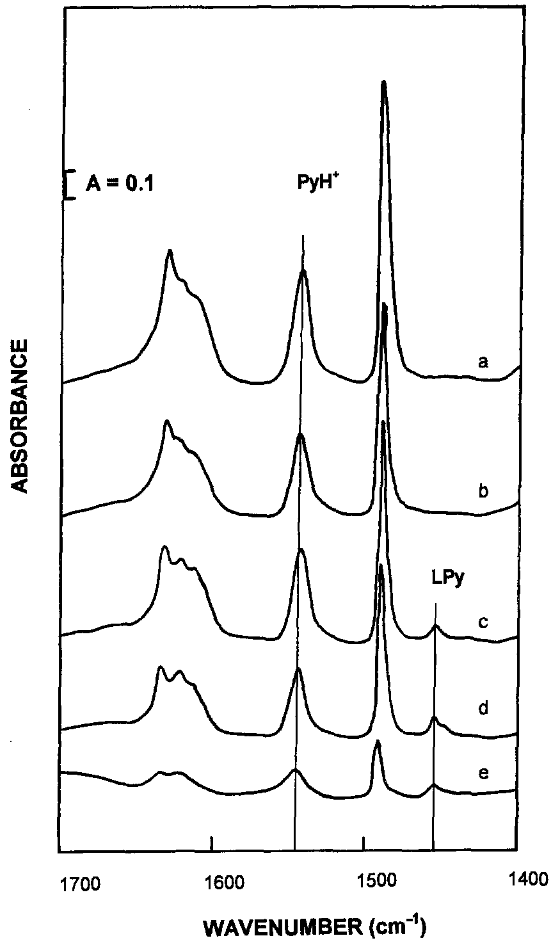

Fig. 2. IR spectra, in the region characteristic of adsorbed pyridine vibrations, of HY samples containing (a) 56 Al/u.c., (b) 36 Al/u.c., (c) 25 Al/u.c., (d) 19 Al/u.c., (e) 5 Al/u.c., after pyridine sorption and evacuation at 423 K.

cm^{-1} (fig. 2). For samples dealuminated by $SiCl_4$, the appearance of a band at about 1450 cm^{-1} (LPy) indicates the presence of Lewis acid sites associated with the extraframework Al-rich phase formed upon dealumination. This band has the strongest intensity for the sample containing the highest amount of extraframework species, i.e. HY-4.8. Assuming the molar extinction coefficient of the 1450 cm^{-1} is equal to 1.5 cm μmol^{-1} [12], the number of pyridine molecules bound to Lewis sites was evaluated for HY-4.5, -4.8, -11.1 samples and found equal to 1.5, 2.2 and 1.1 Lpy/u.c., that is a small amount regarding the high amount of extraframework Al (more than 10 Al/u.c.).

The number of PyH^+ ions formed upon pyridine sorption and evacuation at 423 K was calculated for each sample. It was assumed that one pyridine molecule interacts with one OH group forming one pyridinium ion. For the parent HY sample, the number of PyH^+ species formed upon pyridine sorption and evacuation at 423 K is strictly equal to the number of HF hydroxyl groups since no interaction with LF hydroxyls can be observed. According to neutron diffraction results [3], the number of protons siting in the supercages (HF protons) is equal to 29 per unit cell. This provided a means to determine the molar extinction coefficient of the 1540 cm^{-1} band (characteristic of PyH^+ species) by measuring the integrated intensity of the band. A value of 0.81 cm μmol^{-1} was found, very close to that previously reported [12,13].

The number of PyH^+ species formed upon pyridine sorption and evacuation at 423 K was thus calculated and compared in fig. 3 to the framework Al content, that is the total number of structural OH groups contained by the different HY samples and determined from NMR data. At low Al composition (less than 25 Al/u.c.), the number of PyH^+ ions features exactly the total number of HF and LF protons available while it reaches a plateau at higher Al composition. Clearly, this plateau indicates the saturation of the supercages by pyridinium ions and corresponds to the formation of 29 PyH^+ ions per unit cell, i.e. 3.6 PyH^+ ions per supercage. On purely steric arguments, it may be assumed that the filling of the supercage by pyridine molecules is not complete when forming only 3.6 PyH^+ ions per supercage. In fact, additional pyridine molecules can be adsorbed in HY supercages in the presence of residual pressure of pyridine at room temperature. These molecules were found to interact with LF hydroxyls and form protonated pyridine–LF complexes, exhibiting much less stability than PyH^+ species [5]. The adsorption of benzene, a molecule of about the same kinetic diameter as pyridine, has been studied by Su et al. [14]. It was found that the maximum amount of benzene interacting with hydroxyls of HY zeolite was 4.8 molecules per supercage and this corresponded to the adsorption capacity of faujasite zeolite [14]. Therefore, *purely steric effects alone cannot explain this limit of 3.6 PyH^+ ions per supercage and electrostatic constraints have to be involved.* The main consequence is that the ability of LF hydroxyls to form pyridinium ions, and therefore their acidic character, strongly depends on

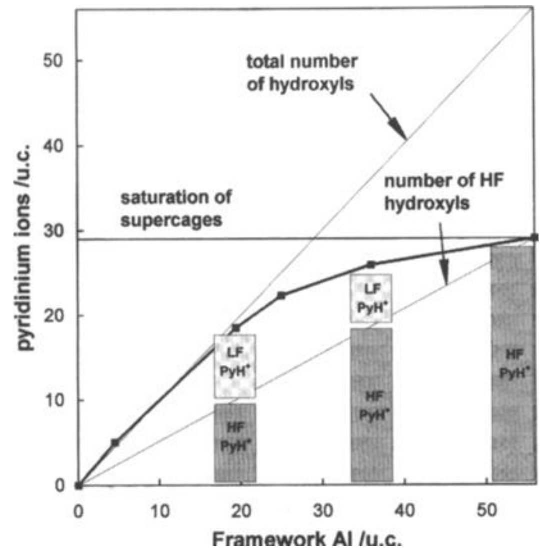

Fig. 3. Number of pyridinium ions versus framework Al composition.

the free available volume in the supercage after saturation of HF sites by pyridine. For the parent HY sample, LF hydroxyls have been shown to partially interact with pyridine through a weak bonding [5]. For the dealuminated sample containing 36 Al/u.c., the saturation of HF sites would correspond to the formation of 19 PyH^+ ions per unit cell. It is therefore expected that some LF sites are allowed to interact with pyridine to form additional PyH^+ ions in the limit of a total number of 29 PyH^+ ions formed per unit cell, which is clearly observed in fig. 1B. For samples for which the total number of protons per unit cell is less than 29, steric and electrostatic constraints are not limiting and HF and LF hydroxyls can both form pyridinium ions. We demonstrate here that the quantitative evaluation of Brønsted acid properties in zeolites by the use of probe molecules strongly depends on both steric and electrostatic effects.

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