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Pyrrole as an NMR probe molecule to characterise zeolite basicity

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The ^{1}H NMR chemical shift of the N–H group of pyrrole adsorbed on alkali metal ion exchanged FAU-type zeolites depends on the zeolite intrinsic basicity, while, as shown for zeolite LiY, the NMR of alkali metal nuclei reflects the interaction of the aromatic cycle with the cations at sites SII.

Zeolite molecular sieves have been extensively investigated mainly due to their application as acidic catalysts in the chemical and petrochemical industry. The large social and economical impact of such processes when compared with those using base catalysts can explain why much less attention has been paid to zeolite basicity. Only recently it has been realized that basic zeolites can also be successfully used as catalysts and have gained a growing interest in the last decade.[1,2]

Basic zeolites are, by definition, non-protonic, and the negative charge created by the presence of aluminium atoms into the network are compensated by extraframework usually monovalent metal cations. The zeolite oxygen atoms act as Lewis basic sites, while the compensating cations act as Lewis acid sites, forming an acid–base pair. The so-called intrinsic zeolite basicity increases with the negative charge on the oxygens, which is determined by their framework structure and chemical composition. The basic strength of zeolites is strongly enhanced by increasing the framework aluminium content, and for a given Si/Al molar ratio, when the electronegativity of the compensating cation decreases. These results can be understood in terms of the average charges over oxygen atoms calculated using the Sanderson principle of equalization of electronegativities based on the zeolite chemical composition.[3] whereas the effect of the crystalline structure was quantified by the more sophisticated electronegativity equalization method (EEM).[4]

The most used method to characterize zeolite basicity uses pyrrole as an IR probe molecule and is based on the shift to lower frequencies of the pyrrole N–H stretching band when the framework basicity increases.[1] Pyrrole is an amphoteric molecule which can interact with zeolite basic sites forming hydrogen bonds between the N–H group and framework oxygen atoms, and with cationic acid sites by donation of charge from its aromatic five-membered heterocycle. Hydrogen bonding is clearly shown by the shift of the IR N–H stretching frequency, while the pyrrole–cation interaction is only suggested from the IR CH out of plane deformation bands[5,6] and by theoretical calculation,[6,7] however, no direct experimental evidence has been reported so far. Here, we show that the ^{1}H NMR chemical shift of the N–H group of pyrrole adsorbed over basic zeolites is a very sensitive probe to measure the average intrinsic basicity, with the advantage that the NMR spectra of alkali metal nuclei provides direct information about the pyrrole–cation interaction, as illustrated for zeolite LiY.

The chemical composition of the zeolites X and Y used here were described previously.[8] Zeolites LiY, KY, CsY and LiX, KX also contains Na$^+$ as compensating cation owing to incomplete exchange. Samples were heated under dynamic vacuum at 673 K for 12 h up to a final pressure of $< 10^{-5}$ kPa, then contacted with the vapor pressure of pyrrole at room temperature for 5 min and subsequently evacuated at 338 K for 30 min to eliminate physisorbed pyrrole.

The ^{1}H NMR spectra of adsorbed pyrrole (Fig. 1), shows three peaks of relative intensity 1:2:2 corresponding to the three types of protons in the molecule. The less intense peak is due to the N–H group, whereas the other two are from the four C–H protons in the five-membered heterocycle; the two C–H groups in α and the two in β positions give rise to the intermediate and high field resonances, respectively. The N–H peak of liquid pyrrole appears at δ 7.1 and shifts to higher frequency when it is adsorbed on alkali zeolites X and Y, to an extent that depends on the sample. From the chemical composition and the characterization performed by other methods, the intrinsic basicity of the zeolites used here increases in the order LiY < NaY < KY < LiX < CsY < NaX < KX.[8] Therefore, the N–H proton resonance shifts to higher frequency when the framework basicity increases, giving differences of up to 3 ppm between LiY and KX (Fig. 1). This shift can be understood by the higher polarization of the N–H bond, which forms hydrogen bonds with the framework oxygen atoms, when the intrinsic zeolite basicity increases.

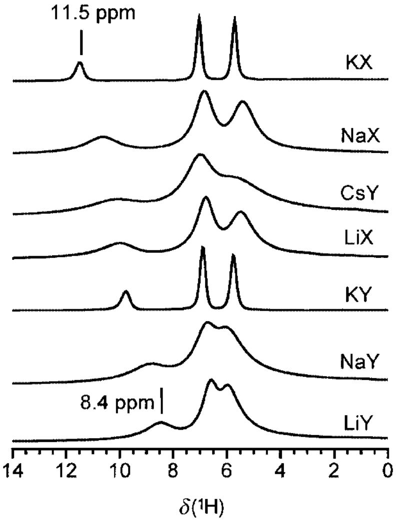

Fig. 1 ^{1}H magic angle spinning (MAS) NMR spectra of pyrrole adsorbed over the zeolites indicated. The samples were prepared by the method described in the text and transferred into the rotors in a glove box. The spectra were recorded at room temperature with a Varian VXR-S 400-WB spectrometer at 399.9 MHz, using a VT CP/MAS Varian probe with 5 mm silicon nitride rotors spinning at 13 kHz. π/2 rad pulses of 6 μs and a recycle delay of 5 s were used.

At the same time, solid state NMR of alkali metal cations reveals their interaction with the guest molecules as illustrated in Fig. 2 for zeolite LiY, where the degassing temperature after the pyrrole adsorption was varied. Very recently, an upfield shift of the ^{7}Li resonance has been reported to occur after the adsorption of benzene over Li-ZSM-5 as a result of 1:1 π-complexation between Li$^+$ and benzene, as confirmed by *ab initio* calculation of ^{7}Li chemical shifts.[9] Fig. 2(a) shows the ^{7}Li NMR spectrum of bare LiY, consisting of a peak formed by two

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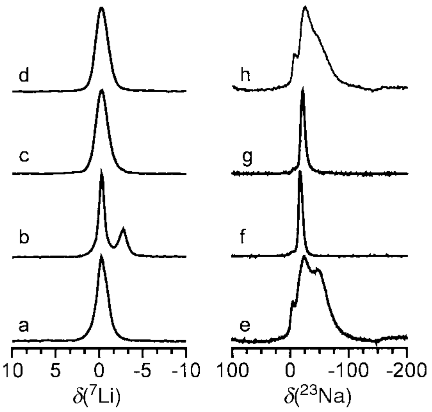

Fig. 2 ^{7}Li and ^{23}Na magic angle spinning (MAS) NMR spectra of: (a) and (e) bare zeolite LiY. Sample LiY after the adsorption of pyrrole at room temperature and evacuation at: (b) and (f) 338 K; (c) and (g) 423 K; (d) and (h) 473 K. The ^{7}Li and ^{23}Na spectra were recorded at room temperature with a Varian VXR-S 400-WB spectrometer at 155.4 and 105.8 MHz, respectively, using a VT CP/MAS Varian probe with 5 mm silicon nitride rotors spinning at 13 kHz. To record both ^{7}Li and ^{23}Na MAS NMR spectra, pulses of 1.5 μs to flip the magnetization $\pi/8$ rad and a recycle delay of 1 s were applied. ^{7}Li and ^{23}Na chemical shifts are referred to 0.1 M solutions of LiCl and NaCl, respectively.

overlapping signals at δ −0.2 and −1.0 which can be assigned to lithium atoms in front of six-ring windows at sites SI′ and SII in the sodalite and super-cages, respectively, of the faujasite structure, in agreement with published results for LiX.[10] From chemical analysis and NMR results the site occupancy per unit cell in zeolite LiY is 24 Li$^+$ at site SI′ and 10 at SII positions. As shown in Fig. 2(b), after pyrrole adsorption and subsequent evacuation at 338 K, the peak from ^{7}Li cations at sites SI′ remains at the same position, while the resonance from ^{7}Li atoms at sites SII shifts to δ −2.8 indicating the direct interaction of accessible Li cations with the π electrons of the pyrrole ring. As is apparent from Fig. 2(c), these pyrrole species are desorbed at 423 K and the original ^{7}Li spectrum is recovered. The corresponding ^{23}Na MAS NMR spectra are shown in Fig. 2(e)–(h). The ^{23}Na spectrum of bare LiY [Fig. 2(e)] shows a peak at δ −3 for cations within the hexagonal prism at site SI, and two broad bands from quadrupolar signals of sodium at sites SI′ and SII.[11] The site population per unit cell is *ca.* 0.8 Na$^+$ at SI and 20 Na$^+$ atoms at sites SII and SI′ (with a higher population of SII). After the adsorption of pyrrole, the signal from Na$^+$ at sites SI remains unchanged while the quadrupole coupling constant (QCC) of sodium atoms at sites SII and SI′ strongly decreases, as shown in Fig. 2(f). Consistent with the results for ^{7}Li, the modification of the ^{23}Na NMR signal of cations at sites SII must be attributed to direct interaction with the aromatic system of the pyrrole molecules. The changes observed for the ^{23}Na signal of Na$^+$ at site SI′, which are inaccessible to pyrrole molecules, could be attributed to the influence of pyrrole adsorption on nearby oxygen atoms, or interpreted in terms of cation migration to accessible positions.[12] The ^{23}Na spectrum of bare LiY zeolite is almost recovered and only some residual pyrrole is evident after evacuation at 473 K [Figs. 2(f)–(h)]. Simultaneously, the ^{1}H resonance of the pyrrole N–H group progressively shifts to higher frequency (up to 0.5 ppm) when the degassing temperature is increased to 473 K, indicating that pyrrole species at more basic sites remain.

The results reported here confirm the model proposed for the adsorption of pyrrole over alkali metal exchanged zeolites of FAU-type structure based on theoretical calculations.[6,7] Pyrrole adsorbs on zeolites Y at cations at sites SII by interaction of its aromatic ring, and the N–H group points towards framework basic oxygen sites forming hydrogen bonds.[6,7] For zeolite LiY, basic centres involving SII sites occupied by Na$^+$ are more basic than those occupied by Li$^+$, although the overall intrinsic zeolite basicity is also modified by the type of compensating cation. Heterogeneity of the basic sites is directly observed by the appearance of several components in the N–H stretching band of pyrrole adsorbed over basic zeolites,[1,13] which are not reflected in the ^{1}H MAS NMR spectra because of the different time scale of both spectroscopic techniques. However, the interpretation of the IR spectra is still controversial,[7,13] and the use of solid state NMR can shed some light in the knowledge of the host–guest interactions between the probe molecules and basic zeolites and the nature of the adsorbed species.

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