FARADAY

Use of but-1-yne as a probe for the characterization of the basicity of alkali-exchanged zeolites

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But-1-yne has been adsorbed at room temperature on a series of LiNa, Na and CsNaX and Y zeolites and also on CsNaX,9Cs and CsNaY,9Cs samples containing nine Cs atoms occluded by a unit cell. An IR study of the 3000–2800 cm^{-1} frequency range clearly showed that but-1-yne isomerized into but-2-yne on CsNaX,9Cs whereas the observation of a band near 1950 cm^{-1} in the case of CsNaY,9Cs characterized the formation of buta-1,2-diene. Such partial transformation of but-1-yne to isomers did not occur on LiNa and Na samples, allowing one to study the basicity of such zeolites from the $\nu(\equiv CH)$ shift which decreases in the following order: NaX > LiNaX > NaY > LiNaY. The main feature is the observation of at least two perturbed $\nu(\equiv CH)$ bands for the NaX and NaY samples, revealing the heterogeneity of the basic sites. This result is discussed taking into account the presence of cations in different positions.

The growing interest in the study of the basic properties of alkali exchanged zeolites is due to their potential application in catalysis, particularly in fine organic chemistry.[1] In order to understand these catalytic properties, it is of great importance to characterize their basicity, *i.e.* the assessment of the strength, the concentration and the nature of basic sites. If IR spectroscopy of adsorbed probe molecules, like pyridine or carbon monoxide, is very often used to characterize the surface acidity of oxides and zeolites,[2] the method is not so convenient to apply to basic materials since no probe can be universally used.[3] However, recently, some papers reported interesting results obtained using pyrrole,[4,5] chloroform[6] and acetylene derivatives.[7] If it was previously shown that pyrrole adsorption is complex, since non-dissociatively and dissociatively adsorbed species can be formed,[8] the first results published by Uvarova *et al.*[7] look very promising, in particular, those relative to the use of acetylene whose $\nu(\equiv CH)$ frequency appears sensitive to the strength of basic sites of a series of sodium zeolites.

The aim of the present paper is to determine to what extent an acetylene compound can be used as a probe of basicity for a series of different alkali exchanged zeolites. In addition to the overall characterization of basicity, we focus on the heterogeneity of the basic sites of the different compounds used and the results are compared to those obtained with chloroform.[6]

In order to overcome the difficulty due to the presence of two coupled $\nu(\equiv CH)$ vibrations in acetylene, we use but-1-yne, $CH_3CH_2C\equiv CH$, as a probe. Its IR spectrum in solution was carefully studied by two of us some time ago,[9] as was also its adsorption on ZnO[10] and Al_2O_3.[11] It should be noted that but-1-yne partly dissociates on both oxides, the lack of the $\nu(\equiv CH)$ vibration preventing the use of but-1-yne as a probe to determine the basicity of these two oxides.

The materials used in the present study are faujasite type zeolites (X and Y) exchanged with different alkali cations. It is known from literature that their basicity increases in the following order:[12] Li-FAU < Na-FAU < K-FAU < Cs-FAU. Moreover X zeolites are more basic than the corresponding Y ones. To improve the basicity of the most basic Cs-FAU zeolite, the encapsulation of Cs_2O in its framework cavities has been carried out.[13,14] Therefore but-1-yne has been chemisorbed on a wide range of basic zeolite materials.

Experimental

Catalyst preparation

Zeolites NaX Linde (Si/Al = 1.21) and NaY Katalistiks (Si/Al = 2.55) were used as starting materials. Prior to modification, the samples were treated with 0.25 M NaCl to remove cations other than Na^+ and to bring the Al/Na ratio to equilibrium. The obtained samples were used in studies as parent NaX and NaY zeolites.

Exchange. Lithium forms of X and Y zeolites were prepared by conventional cation-exchange procedures with a 0.1 M solution of $LiNO_3$ at room temperature (r.t.). For the caesium exchange, sodium cations in NaX and NaY were exchanged at r.t. with 0.1 M solution of caesium acetate. Three exchanges were performed, the first two for 24 h time periods, the third for 48 h. Then the catalysts were filtered and rinsed with deionized water and dried at 373 K for 5 h. The degree of Na^+ to Li^+ or Cs^+ exchange, obtained from atomic absorption spectroscopy, allows one to determine the formula of the compounds so prepared: $Li_{30}Na_{55}(AlO_2)_{86}(SiO_2)_{106}$ (LiNaX), $Li_{22}Na_{32}(AlO_2)_{54}(SiO_2)_{138}$ (LiNaY), $H_xCs_{32}Na_{41}(AlO_2)_{86}(SiO_2)_{106}$ (CsNaX) and $H_xCs_{30}Na_{19}(AlO_2)_{54}(SiO_2)_{138}$ (CsNaY). A partial decationisation could occur during preparation of caesium samples.

Impregnation. The so-obtained CsNaX and CsNaY samples, calcined at 673 K for 2 h, were wetted in a dry box by a precalculated volume of 0.2 M caesium acetate in order to obtain nine caesium acetate molecules per unit cell, following the procedure described in ref. 14. After evacuation at r.t. in an evaporator, the temperature was raised to 313 K (3 h) and 353 K (2 h) to remove bulk water and leave caesium acetate occluded in the zeolites. The samples were then calcined at 673 K for 2 h. The so-obtained samples are denoted CsNaX,9Cs and CsNaY,9Cs (nine Cs atoms occluded per unit cell).

X-Ray analyses indicated that the crystallinity of all prepared samples was largely retained.

IR experiments

Zeolite samples were pressed into self-supported wafers (*ca.* 15 mg with diameter of 16 mm). They were activated *in situ* at

673 K under vacuum for 5 h. Portions of $CH_3CH_2C{\equiv}CH$ were then introduced at room temperature. All the spectra were recorded on a Nicolet 60-SX spectrometer. The spectrum of the activated catalyst was automatically subtracted in order to obtain that of the adsorbed species formed.

Results

The spectrum of species formed upon adsorption of large amounts of but-1-yne on LiNaY is shown in Fig. 1. It mainly presents bands at 3290 [$\nu(\equiv CH)$], 2986 [ν_a, $\nu_s'(CH_3)$], 2946 [$\nu_s(CH_3)$], 2927 [sh, $\nu(CH_2)$], 2887 [2 $\delta(CH_3)$], 2153, [vw, $\omega(CH_2) + \nu_s(CCC)$], 2105 [$\nu(C{\equiv}C)$], 1462 [$\delta_a$, $\delta_s'(CH_3)$], 1438 [$\delta(CH_2)$], 1384 [$\delta_s[CH_3)$] and 1319 cm^{-1} [$\omega(CH_2)$]. All these values are very close to those reported for but-1-yne in solution.[9] However, when very small doses of but-1-yne are introduced (30 μmol g^{-1}), a shoulder near 3250 [$\nu(\equiv CH)$] and another near 2097 cm^{-1} [$\nu(C{\equiv}C)$] are noted (Fig. 2). We do not observe any band higher than 3300 cm^{-1}, assignable to an OH group, resulting from a dissociative but-1-yne adsorption. We conclude that no dissociation occurs, in contrast to that observed before on metal oxides.[10,11]

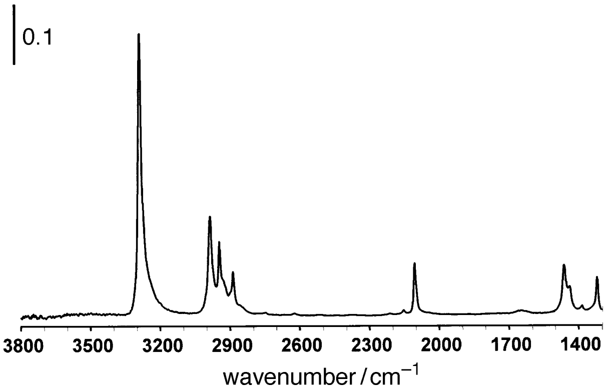

Fig. 1 IR spectra of species formed from but-1-yne introduction (1 mmol g^{-1}) on LiNaY

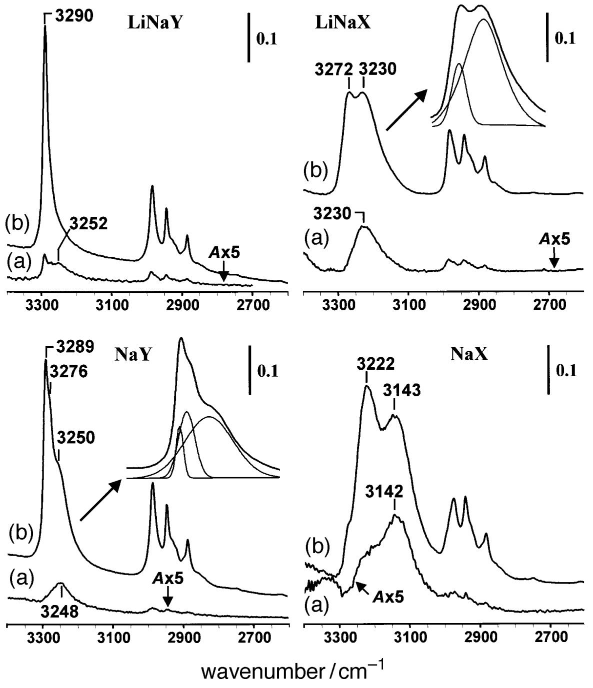

Fig. 2 IR spectra of species formed from but-1-yne introduction (30 μmol g^{-1}) (a) then 1 mmol g^{-1} (b) on LiNaY, NaY, LiNaX and NaX

LiNa and Na faujasites

Fig. 2 shows in the 3400–2700 cm^{-1} range the spectra of species formed when a small (30 μmol g^{-1}) or a large amount (1 mmol g^{-1}) of but-1-yne was introduced on LiNaY, NaY, LiNaX and NaX.

If the results obtained on LiNaY are simple since mainly a sharp $\nu(\equiv CH)$ band with a weak shoulder at 3252 cm^{-1} is observed, those relating to the other zeolites are more complex. When a large amount of but-1-yne is introduced, two $\nu(\equiv C{-}H)$ bands (LiNaX, NaX) or even three (NaY) are clearly apparent (Fig. 2). That at low wavenumber (LW), first appears when a small amount of but-1-yne is added, suggesting it corresponds to but-1-yne adsorption on the most basic sites. Its wavenumber decreases in the following order: LiNaY (3252) > NaY (3248) > LiNaX (3230) > NaX (3142 cm^{-1}).

The same order is observed for the high wavenumber (HW) band: LiNaY (3290) > NaY (3289, 3276) > LiNaX (3272) > NaX (3222 cm^{-1}).

The wavenumber of the bands in the range below 1600 cm^{-1} is quite similar to that reported above in the case of LiNaY. As for the $\nu(C{\equiv}C)$ band, its wavenumber is situated near 2095–2097 cm^{-1}. A shoulder is noted at 2105 cm^{-1} when a large amount of but-1-yne is introduced on NaY.

Cs compounds

But-1-yne adsorption on CsNaY leads to the appearance of two $\nu(\equiv CH)$ bands, one at 3278 (sharp) the other at 3258 cm^{-1} with probably a broad shoulder near 3225 cm^{-1} (Fig. 3). In contrast to the results reported above, their intensity increases almost in unison. When the first amounts of but-1-yne are introduced, the $\nu(C{\equiv}C)$ band is first observed at 2096 cm^{-1} and its wavenumber shifts to 2103 cm^{-1} by adding more but-1-yne. The bands below 1600 cm^{-1} are similar to those reported above.

An important point is the relative intensity of the main $\nu(CH)$ bands observed at *ca.* 2975, 2938 and 2882 cm^{-1}: that at 2938 cm^{-1} is the most intense whereas that at *ca.* 2980 cm^{-1} predominated in the case of LiNa and Na faujasites (Fig. 1 and 2).

The spectrum for the $\nu(CH)$ range when adsorbing but-1-yne on CsNaX is similar to that reported for CsNaY but is even more complex since for instance the 2975 cm^{-1} band presents two shoulders at *ca.* 2989 and 2966 cm^{-1}. As for the $\nu(\equiv CH)$ vibration, it gives rise to a very broad band near 3230 cm^{-1}. Below 2300 cm^{-1}, the spectrum is similar to that observed for CsNaY.

The results obtained on CsNaY, 9Cs are quite different (Fig. 4). (i) A broad $\nu(\equiv CH)$ band at 3254 cm^{-1} is accompanied by a rather sharp shoulder at 3276 cm^{-1}. (ii) The spectrum in the $\nu(CH)$ range changes with the amount of but-1-yne introduced. Four main bands are observed at 2971, 2937, 2924 and

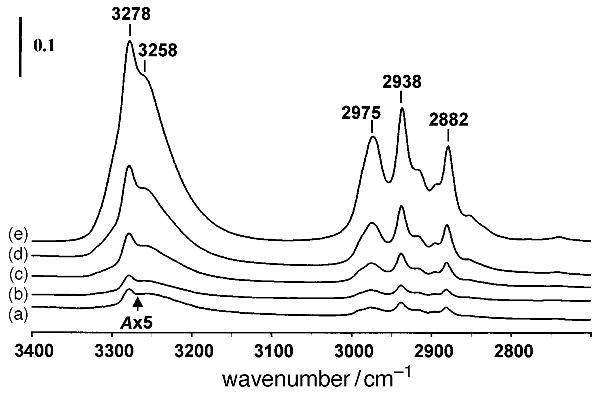

Fig. 3 IR spectra of species formed from but-1-yne introduction [15 (a), 90 (b), 190 (c), 380 (d) and 900 (e) μmol g^{-1}] on CsNaY

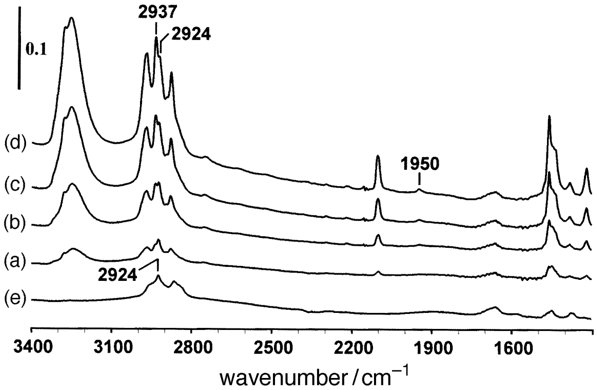

Fig. 4 IR spectra of species formed from but-1-yne introduction [160 (a), 300 (b), 630 (c), 1000 (d) μmol g^{-1} followed by evacuation at r.t. (e)] on CsNaY,9Cs

2879 cm^{-1}, but the relative intensity of those at 2937 and 2924 cm^{-1} changes with the amount of probe added, that at 2924 cm^{-1} being first predominant and later becoming a shoulder of that at 2937 cm^{-1}. Moreover, after evacuation of but-1-yne at room temperature, ν(CH) bands as that at 2924 cm^{-1} persist whereas no $\nu(\equiv$CH) is visible. (iii) In the region below 2300 cm^{-1}, in addition to the bands observed from but-1-yne adsorption on the other zeolites, a weak band near 1950 cm^{-1} is noted. Moreover, in addition to the 1460 and 1435 cm^{-1} bands, a broad band appears at *ca.* 1447 cm^{-1} which persists after evacuation at r.t., with two other broad bands at *ca.* 1370 and 1378 cm^{-1} (Fig. 4).

Interestingly, introduction of but-1-yne to CsNaX,9Cs does not lead, for the first doses introduced, to any $\nu(\equiv$CH) band, nor to a ν(C$\equiv$C) band, whereas three well resolved ν(CH) bands at 2960 (medium), 2922 (strong) and 2866 cm^{-1} are clearly observed (Fig. 5). It is only when a large amount of but-1-yne is introduced (400 μmol g^{-1}) that a $\nu(\equiv$CH) band clearly appears at 3210 cm^{-1} along with a ν(C$\equiv$C) bond at 2100 cm^{-1}. In the region below 1500 cm^{-1}, the spectrum is also very different from the previous ones since only one sharp band is noted at *ca.* 1430 cm^{-1} whatever the amount of but-1-yne introduced.

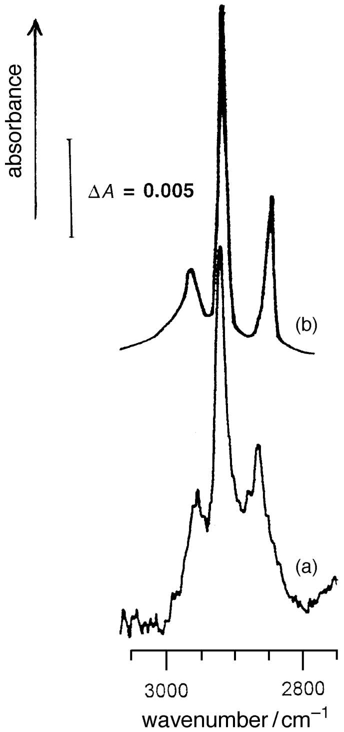

Fig. 5 Comparison of IR spectrum (2800–3000 cm^{-1}) of species formed from but-1-yne adsorption on CsNaX,9Cs (a) with that of the ν(CH$_3$) bands of but-2-yne in the liquid state (b)

Discussion

Spectra assignment: but-1-yne reactivity

The spectra obtained adsorbing but-1-yne on LiNa and Na faujasites in the ν(CH) (3000–2700 cm^{-1}) and δ(CH) ($\nu < 1500$ cm^{-1}) ranges are close to those of but-1-yne in solution. However, we note that for LiNaX and NaX (Fig. 2) that the ν(CH) bands are broader than those observed for LiNaY and NaY. As we will see later, this could be due to a strong interaction of but-1-yne with the X zeolites and also to the formation of at least two species.

Results obtained on Cs compounds are more surprising. Let us consider first the case of CsNaX,9Cs. ν(CH) bands are found for the first doses of but-1-yne introduced whereas no $\nu(\equiv$CH) and ν(C$\equiv$C) bands are observed. This result can be explained considering the formation of but-2-yne from isomerization of but-1-yne, since the spectrum of but-2-yne in the considered frequency ranges agrees very well with that reported in Fig. 5. In CCl$_4$ solution, ν(CH$_3$) bands are noted at 2964 (ν_a), 2919s (ν_s), 2848 (2ν_a) and 2735 cm^{-1}, [vw, 2δ_s], whereas in the δ(CH$_3$) range, the main band occurs at 1435 cm^{-1} (δ_a), that at 1375 cm^{-1} (δ_s) being very weak. Note, owing to the presence of a center of symmetry, that no ν(C$\equiv$C) is clearly observed by IR spectroscopy.

This means that when in contact with CsNaX,9Cs, but-1-yne isomerization is fast at room temperature. We note that a similar isomerization has been reported on basic oxides, such as ZnO, on which intermediate species of the propargylic type have been detected.[10]

The formation of but-2-yne, which is less evident on the other Cs compounds, can explain the complexity of the spectra observed in the ν(CH) range. It is worth noting that an intermediate compound from but-1-yne to but-2-yne isomerization is buta-1,2-diene, the IR spectrum of which presents a band near 1950 cm^{-1}, as observed from but-1-yne adsorption on CsNaY,9Cs (Fig. 4). In such a case the isomerization would not be so complete. This compound readily gives rise to polymers, which explains the fact that after evacuation at r.t. some ν(CH) remains whereas no $\nu(\equiv$CH) band is observable (Fig. 4).

We therefore conclude that the partial transformation of but-1-yne to isomers on Cs zeolites prevents any useful information from the study of the $\nu(\equiv$CH) range. Taking into account that X zeolites are more basic than Y ones, as also shown below, and that zeolites with encapsulated Cs$_2$O are more basic than zeolites without Cs$_2$O, the analysis of the spectra tends to show that the degree of isomerization of but-1-yne increases with the zeolite basicity.

Basicity of LiNa and Na faujasites

The two main $\nu(\equiv$CH) bands observed in the series of spectra reported in Fig. 2 indicate the presence of basic sites with different strengths in the compounds studied. Our results relative to NaY and NaX seem clearer than those reported in ref. 7 using acetylene as a probe. This is certainly due to the presence of two $\nu(\equiv$CH) vibrations in acetylene, which are strongly coupled, the perturbation of one modifying the frequency of the other. Note that pyrrole adsorption on LiY, NaY, LiX and NaX led to one broad ν(NH) band located at 3435, 3390, 3295 and 3280 cm^{-1}, respectively, indicating the same order of basicity as reported here.[15] We also note that for pyrrole adsorption on an NaX sample, an asymmetric hydrogen double-well potential has been suggested.[8] The complexity of the spectrum observed suggested the formation of a C$_4$H$_4$NH $\cdots$ O hydrogen bonded species of pyrrole adsorbed on weak basic sites and the formation of a C$_4$H$_4$N$^-$ $\cdots$ $^+$HO species adsorbed on relatively strong basic sites. The present results confirm the coexistence of both type of sites and so the heterogeneity of zeolite basic sites.

Note that Huang and Kaliaguine[15] by computer deconvolution of the perturbed ν(NH) band of pyrrole suggested the existence of three individual ν(NH) components. Fig. 2 indicates that such a number of components is apparent when but-1-yne is used in the case of NaY and possibly also NaX, if a weak shoulder near 3280 cm^{-1} is taken into account. Spectral deconvolution is quite easy when but-1-yne is used (Fig. 2), in contrast to pyrrole,[4,5] allowing us to conclude that the former probe is more informative than the latter.

Chloroform adsorption on a similar series of zeolites[6] led to the same order of basicity from the ν(CH) frequency which decreased when the basicity increased: LiNaY (3028 cm^{-1}) < NaY (3017 cm^{-1}) < LiX (3016 cm^{-1}) < NaX (2995 cm^{-1}). However, for these compounds, only one band was observed, showing again that the use of but-1-yne is more informative concerning site heterogeneity. By contrast, chloroform adsorption on K, Rb, Cs faujasites led to determination of the basicity of these materials without taking into account any decomposition or rearrangement.

Complexation of 1-alkynes with bases has been studied by IR spectroscopy in solution.[16] It is interesting to compare the results obtained with those reported in the present study. We note that the $\nu(\equiv CH)$ wavenumber of 1-alkynes in the liquid phase (3292–3000 cm^{-1}) is close to that observed for but-1-yne adsorbed on LiNaY showing that the basicity of this zeolite is quite low. The $\nu(\equiv CH)$ wavenumber of the HF band for LiNaX (3272 cm^{-1}) and NaY (3289, 3276 cm^{-1}) indicates an interaction similar to that reported for 1-alkynes with ketones ($pk_b = 21$) whereas those of the LF band of LiNaX (3230 cm^{-1}) and HF band of NaX (3222 cm^{-1}) are not very different from that resulting from the interaction of 1-alkynes with pyridine ($pk_b = 8.8$). Finally the value of 3143 cm^{-1} characterizing the LF band for NaX is very low, much lower than that reported for 1-alkynes interacting with trimethylamine (3206 cm^{-1}, $pk_b = 4$) indicating that the corresponding basicity is quite high. In agreement with results obtained in solution,[16] the present results show that the $\nu(C\equiv C)$ band is almost insensitive to $CH_3CH_2C\equiv C-H \cdots OZ$ interaction.

As for the relative number of basic sites for each zeolite studied, we do not think it is possible to deduce this directly from the intensity of the $\nu(\equiv CH)$ components. Indeed, it is well known that, when hydrogen bonding occurs, the intensity of the perturbed band increases with the strength of the perturbation. For instance, it has been reported that the integrated intensity of the $\nu(\equiv CH)$ band is 2.7 times greater when 1-heptyne is complexed to a ketone compared with when it is in CCl_4 solution.[17] Fig. 2 demonstrates such an effect: introduction of the first dose, which is sufficiently small to be considered as completely chemisorbed on all the samples, gives rise to a perturbed $\nu(\equiv CH)$ band much more intense on NaX (Fig. 2). Its intensity decreases in the following order: NaX > LiNaX > NaY, LiNaY mirroring the basicity of the samples. Note that Murphy *et al.*[4] when adsorbing pyrrole on alkali cation exchanged EMT zeolites, directly deduced the relative population of sites from the ν(NH) band intensity characteristic of the interaction, assuming that the molar absorption coefficient ε(NH) is independent of the interaction strength which has yet to be established.

Heterogeneity of sites

Finally, the origin of the heterogeneity of basic sites has to be considered. Previous work showed that IR data relative to pyrrole or chloroform adsorption can be correlated with the oxygen charge calculated from Sanderson's electronegativity.[6,15] It explains the difference observed between X and Y samples, the negative partial charge on zeolite framework oxygens being higher for the former materials, in agreement with the higher frequency shift, $\Delta\nu(\equiv CH)$, observed for X samples.

However, the concept of Sanderson's electronegativity does not explain the heterogeneity of the basic sites observed for NaX and NaY samples (Fig. 2). Murphy *et al.*[4] considered that the Lewis basicity in zeolites is a local property dependent on the nature of the adjacent cations. Since the exchange of Na^+ by Li^+ is incomplete, unexchanged sodium cations in LiNaX and LiNaY samples can induce a basicity close to that observed in the parent samples, which could explain the occurrence of the band at 3230 cm^{-1} for LiNaX, close to that found at 3222 cm^{-1} for NaX, and that at 3252 cm^{-1} for LiNaY, close to that observed at 3250 cm^{-1} for NaY.

The presence of at least two $\nu(\equiv CH)$ perturbed bands for NaX and NaY is proof of the heterogeneity of Lewis basic sites in these zeolites.

The strongest basic sites in NaX involved in the formation of the $\nu(\equiv CH)$ band at 3143 cm^{-1} probably correspond to framework oxygens coordinated with Na^+ in S_{III} positions. It is known that faujasite type zeolites, in which cations occupy S_{III} positions, are able to dissociate compounds such as H_2S [18] and CH_3SH [19] owing to their strong basicity. Sodium cations in S_{III} position are located between O_1 and O_4 zeolite framework oxygens.[1,20]. Their occupation in this position decreases when the Si/Al ratio increases[18] and is not clear in NaY zeolites.[21–23] We could expect a small level of sodium localized in the S_{III} position in NaY, explaining the occurrence of the shoulder near 3250 cm^{-1} (Fig. 2). The higher wavenumber of this band compared to that observed at 3142 cm^{-1} for NaX is due to the general feature reported above, namely that the negative partial charge of the zeolite framework oxygens is lower for Y type zeolites than for X zeolites.

The two other clearly evident IR bands in Fig. 2 for NaX and NaY zeolites could be due to but-1-yne adsorption on framework oxygens adjacent to sodium cations in S_{II} position (*i.e.* coordinated with oxygens in O_2 position and in $S_{I'}$ position [linked to O_3 (ref. 20)].

Exchange of Na^+ by Li^+ changes the cations positions. It is well known from the literature[24] that Li^+ cations prefer $S_{I'}$ positions, localized in the centre of the framework six rings. The maximum occupancy of I′ positions is 32 per unit cell, which is just the limit of the exchange of the studied samples. In this position, cations are coordinated with O_3 oxygens.[1,20] In LiNaX, the S_{III} position is not occupied by either Li or Na cations[24] and is the reason for the lack of any band near 3143 cm^{-1} after but-1-yne adsorption. The presence of a new band at 3272 cm^{-1} (which appears as a shoulder on NaX) when adsorbing but-1-yne on LiNaX (Fig. 2) can be explained due to the following features: (i) the fact that $Li_{I'}-O_3$ distance is shorter than that for Na—O, (ii) the $T-O_3-T$ angle decreases from Na to Li decreasing the oxygen basicity[24] and (iii) as recently shown[4] the strength of the basic sites decreases for the framework oxygens associated with Na^+ cations in the following order: II > I > I′. In LiNaX, $S_{I'}$ positions are fully occupied by lithium cations and the oxygen associated with this position shows the lowest basicity.

Conclusion

The present results show that but-1-yne is a very sensitive probe to study, from the $\Delta\nu(\equiv CH)$ shift, the basicity of zeolites when this basicity is rather weak (LiNaY, NaY, LiNaX, NaX). In particular, it clearly reveals the heterogeneity of basic sites, which is not the case when chloroform is used.[6] This heterogeneity was already reported for EMT zeolites using pyrrole as a probe,[4] but this result was obtained after computer deconvolution of the ν(NH) band which is always difficult to achieve when the band is broad. On more basic zeolites, isomerization occurs which prevents the use of but-1-yne from the spectroscopic point of view at least at r.t. Other probes, like acetylene, in spite of the coupling between the two $\nu(\equiv CH)$ modes, or 3,3-dimethylbut-1-yne which cannot isomerize, would be more convenient. However, but-1-yne isomerization itself could be an interesting reaction to compare the basicity of zeolites, since it has been well known for a long time[25] that this reaction occurs under basic conditions. The present results indeed suggest that the more basic the material (CsNaX,9Cs), the greater the rate of isomerization.

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