NO$_2$ disproportionation for the IR characterisation of basic zeolites

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**NO$_2$ disproportionation on alkaline zeolites is used to generate nitrosonium (NO$^+$) and nitrate ions on the surface, and the infrared vibrations observed are very sensitive to the cation chemical hardness and to the basicity of zeolitic oxygen atoms.**

The reliable and quick characterisation of zeolite basicity has remained up to now a problem, and we propose here a new infrared method using NO$_2$ disproportionation. The formation of NO$^+$ ions in exchange positions on acidic zeolites by the adsorption of NO$_2$ or by the co-adsorption of NO and O$_2$ was reported some time ago.[1] The formation of NO$^+$ on an acid base pair was reported[2] on titanium oxide, with a ν(NO$^+$) band at 2206 cm^{-1}. The direct interaction between the NO$^+$ ion and the zeolitic oxygen atoms leads to an unprecedented sensitivity to the electron density on the framework oxygen atoms, with clearly separated signals for oxygen atoms in the main channel and in the

side pockets of acidic mordenite.[3] We describe here the use of NO$^+$ ions for the study of cationic zeolites.

NO$^+$, nitrate (and nitrite) ions are formed by the disproportionation of NO$_2$ on activated alkaline zeolites.[3,4]

$$2\ NO_2 = N_2O_4 = NO^+ + NO_3^-$$
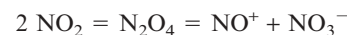
We performed this reaction in an infrared cell on a series of cation exchanged X zeolites (Si/Al = 1.3) detailed in Table 1. Fig. 1 shows the ν(NO$^+$) vibration band in the series of samples and its frequency shift with the nature of the cation. In a very constrained environment, as in the side pockets of mordenite, the ν(NO$^+$) vibration band is shifted to higher wavenumbers.[3] In our experiments, the several possible locations for the NO$^+$ ion in the structure lead to several overlapping bands for the ν(NO$^+$) vibration. By analogy with what was observed in mordenite, we assign the low frequency component of the ν(NO$^+$) vibration band to NO$^+$ ions in the supercages of the faujasite structure. Ionic exchange from a sodium form to another cation is known to take place initially in the supercages[5] (except for the very small Li$^+$ ions,

Table 1 Chemical composition of the X zeolite samples

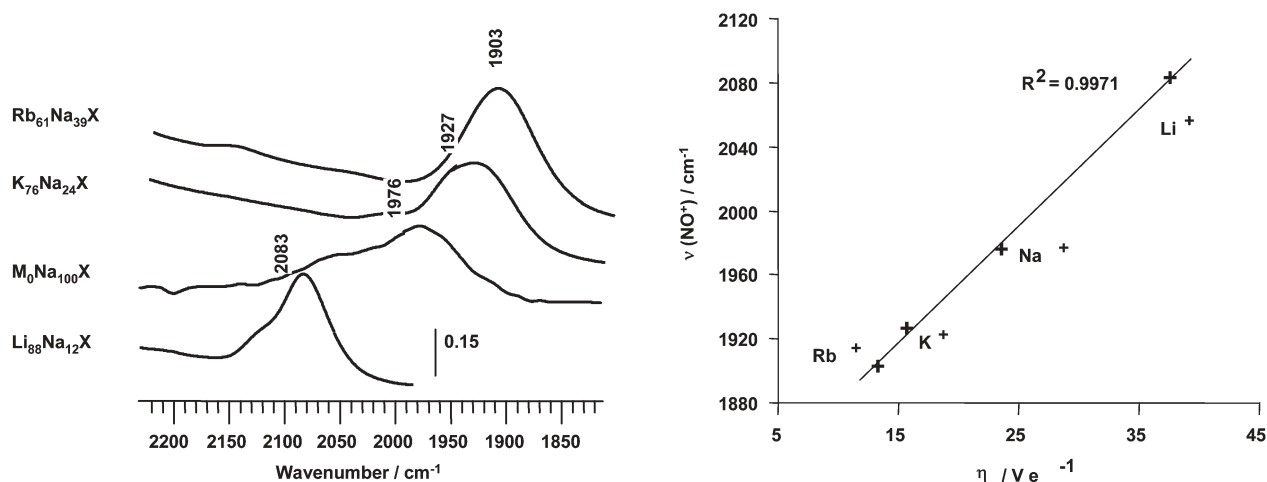| Sample name	Si/Al[a] mol ratio	Na$^+$/Al[a] mol ratio	M$^+$/Al[a] mol ratio	EFAL[a] /mol%	Formula
Li$_{88}$Na$_{12}$X	1.31	0.12	0.86	2	Na$_{10}$Li$_{71}$Al$_{81}$Si$_{111}$O$_{384}$
M$_0$Na$_{100}$X	1.26	0.95	0	5	Na$_{81}$Al$_{81}$Si$_{111}$O$_{384}$
K$_{76}$Na$_{24}$X	1.28	0.23	0.74	3	Na$_{19}$K$_{62}$Al$_{81}$Si$_{111}$O$_{384}$
Rb$_{61}$Na$_{39}$X	1.33	0.37	0.57	6	Na$_{30}$Rb$_{47}$Al$_{77}$Si$_{115}$O$_{384}$

[a] From elemental chemical analysis.

Fig. 1 Left: infrared spectra after NO$_2$ disproportionation at low coverage (3–5 molecules per unit cell) over M$^+$ X zeolites in the ν(NO$^+$) vibration range. Right: frequency of the ν(NO$^+$) vibration band *vs.* cation chemical hardness η as defined in ref. 10.
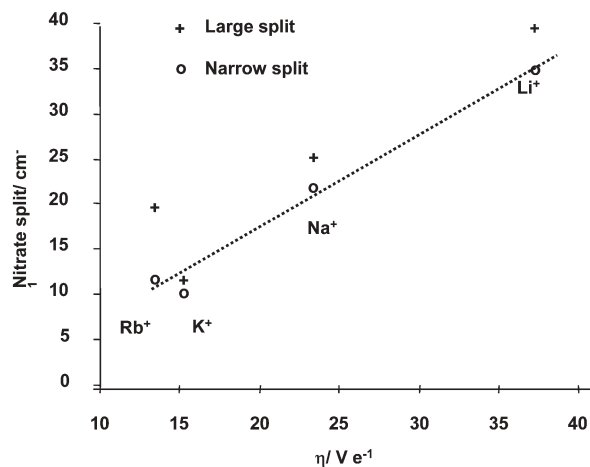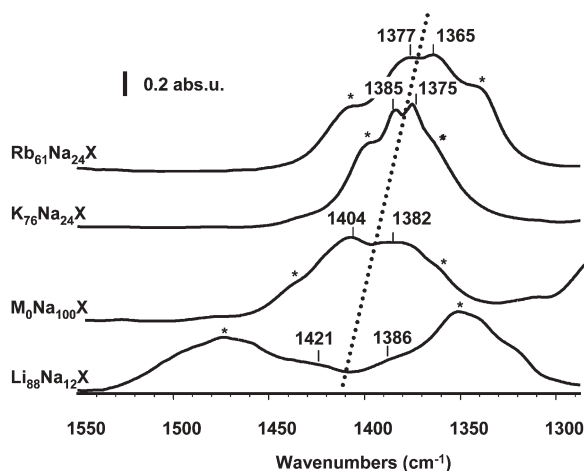
Fig. 2 Left: infrared spectra after NO_2 disproportionation over M^{n+} zeolites in the $\nu(NO_3^-)$ vibration range (at the same low coverage as for Fig. 1). Stars are used to indicate the large split (more intense with Li^+ due to its preferred location in the sodalite units), wavenumbers are indicated for the small split (determined using the second derivative). Right: splits of the nitrate bands *vs.* chemical hardness of the cation (values for the large split divided by 3).

for which the preferred location seems rather to be the sodalite unit) and our samples are all over 60% exchanged. The low frequency component of the $\nu(NO^+)$ vibration band group observed at low NO^+ coverage can thus be used to characterise the exchanged cation in the supercages. We used this very clear low frequency component, and we simply refer to it as the $\nu(NO^+)$ vibration band in what follows.

The basic strength of a zeolite has been linked to the electronic charge on the oxygen atoms (as determined by Sanderson's electronegativity equalisation principle[6] for fully exchanged zeolites) and is expected to be in the following order: RbX > KX > NaX > LiX due to the ionisation potential of the alkaline metal.[7] In our experiments, the $\nu(NO^+)$ frequency is even better correlated to the hardness of the cation[8] (as defined in Fig. 1). Hard atoms or molecules are more difficult to polarize than soft atoms or molecules: in fully exchanged zeolites, harder alkaline cations (Li^+ and Na^+) induce a smaller electronic charge on the framework oxygens than softer cations (K^+ and Rb^+).[9] Here, we observe a linear correlation between the frequency of the $\nu(NO^+)$ vibration band and the hardness of the cation,[10] inversely proportional to the basic strength of each of the oxygen atoms.

NO_2 disproportionation also produces nitrates and nitrites, with infrared bands in the 1600–1200 cm^{-1} region (Fig. 2). The antisymmetric ν_a vibration band of nitrates is a narrow band around 1385 cm^{-1} in highly symmetrical alkaline salts. The loss of symmetry of the nitrates in the electric field inside the zeolite leads to a splitting of the band into a doublet. For each sample, we observe two doublets with different splitting, which we assign to different locations of the nitrate in the zeolite structure. The doublet with the narrower splitting is easier to observe, and its splitting is linearly linked to the $\nu(NO^+)$ vibration frequency in the supercage, and to the polarising power of the cation (Fig. 2). A more polarising cation induces a greater symmetry loss and a greater splitting. The alkaline cation remains thus close to the NO^+ and NO_3^- ions and to the framework oxygen atoms, which gives indications for modelling the ionic complex obtained.

Modelling the interaction of N_2O_4, NO^+ and NO_3^- with alkali metal ions was done using Density Functional Theory (DFT)

calculations.‡ Influence of the zeolite lattice was studied by cluster type calculations, using a double 4 ring model representing the s_{III}' site inside faujasite, terminated by OH bonds (one Al atom: Si/Al = 5, sodium in the cation position). The terminating oxygen atoms were kept fixed at their crystallographic position during geometry optimization. NO^+ and NO_3^- ions are formed ($d(N_1O_1) = 1.128$ Å in NO^+, $d(N_1O_2) = 1.850$ Å in the nitrate, $q(NO^+) = 0.454$ e, $q(NO_3^-) = -0.407$ e). The frequency of the $\nu(NO^+)$ vibration (1972 cm^{-1}) agrees well with the experiment.

These calculations suggest that NO^+ and NO_3^- ions, formed after N_2O_4 adsorption on the basic site of a zeolite, remain closely together, thus interacting with the alkaline cation and the framework oxygen atoms of the zeolite. The complex formed can account for the observed $\nu(NO^+)$ vibration frequency, and shows the influence of the cation on electron density on the framework oxygen atom.

Disproportionation of NO_2 on cation exchanged zeolite (and possibly on other oxides[2]) is thus a powerful tool for the characterisation of the basicity of the framework oxygen atom. A complex is formed between the cation, the anionic framework oxygen atom, NO^+ and NO_3^-. The frequency of the $\nu(NO^+)$ vibration band together with the ionicity of the nitrate (measured by the splitting in the nitrate doublet) are indicative of the chemical hardness of the cation and of the basicity on the oxygen.

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