

Semi-quantitative estimation by IR of framework, extraframework and defect Al species of HBEA zeolites

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A simple method based on the characterization (composition, Brønsted and Lewis acidities) of acid treated HBEA zeolites was developed for estimating the concentrations of framework, extraframework and defect Al species.

The large pore zeolite BEA has been shown to have a great potential as an acid catalyst in various reactions of refining,^{1,2} petrochemicals,^{3,4} and fine chemicals.^{5–8} The generally small size of the synthesized samples, the particular framework structure constituted of the connection of two polymorphs with, as consequence, the presence of many local defects could explain the remarkable catalytic properties of this zeolite.⁸ Three main categories of Al coexist in the protonated form (HBEA): framework Al atoms which are responsible for the strong Brønsted acidity (bridging hydroxyl groups AlOHSi), partially coordinated Al atoms (structure defects)^{8–15} which are Lewis acid sites and extraframework Al (EFAL) species which can be of different types: monomeric to polymeric, neutral or cationic,¹⁶ etc. We show here that acid treatment of HBEA sample allows the quantification of the various Al species.

The HBEA zeolite (Cal) results from calcination under dry air flow up to 550 °C of a NH₄BEA sample (CP814E from Zeolyst International). The acid treatment was carried out under stirring at 30 °C or 100 °C (only one sample) of Cal in a 1 M HCl solution (10 cm³ g⁻¹ zeolite) for different times. The resulting samples were characterized by elemental analysis, XRD, nitrogen adsorption and IR spectroscopy. The position of the structure bands (450–1250 cm⁻¹) and especially that of the asymmetric stretch vibration (ν_{TOT}) at 1080–1200 cm⁻¹ was determined using KBr wafers containing 0.5 wt% of the zeolite sample. The characterization of the OH groups and chemisorbed pyridine molecules was performed using thin wafers of the zeolite samples, pre-treated under air flow at 450 °C for 10 hours then evacuated at *ca.* 10⁻⁶ Torr. The concentration of Brønsted and Lewis sites were calculated from the integrated area, for a temperature of pyridine desorption of 150 °C, of the PyH⁺ and PyL bands at 1545 and 1450 cm⁻¹ respectively, using the values of the extinction coefficients: 1.11 and 1.31 $\mu\text{mol}^{-1}\text{cm}$ determined in a previous study.¹⁷ The use of the same extinction coefficients for the series of acid treated samples can be criticized,¹⁸ nevertheless, it leads to acceptable semi-quantitative data provided that the thickness of the wafers used and the surface areas of the samples are not very different.¹⁹ All these usual precautions were satisfied in this study.

Figs. 1–3 show the effect of acid treatment on the wavenumber of the structure band (ν_{TOT}) and on the Brønsted and Lewis acid sites concentration. On the abscissa are indicated the time *t* of acid treatment and x'_{Al} , the atom fraction of Al in the zeolite.

$$\left(x'_{\text{Al}} = \left(\frac{n_{\text{Al}}}{n_{\text{Al}} + n_{\text{Si}}} \right)_{\text{Total}} \right)$$

A significant decrease in x'_{Al} , *i.e.* a significant elimination of Al atoms from the zeolite, can be observed for short values of *t*: *e.g.* 32 and 54% after 3 and 10 minutes at 30 °C; afterwards, the

dealumination becomes much slower: 66% after 240 minutes *i.e.* 12% only from 10 to 240 minutes. The percentage of dealumination also increases with the temperature of acid treatment: 85% at 100 °C against 66% at 30 °C after 240 minutes.

Two domains can be defined in Fig. 1 and 2:

For $0.036 \leq x'_{\text{Al}} \leq 0.074$ (Domain I) *i.e.* for short *t* values (0–10 minutes), there is no change in ν_{TOT} (Fig. 1) and only a small decrease in the concentration of protonic acid sites (13%) (Fig. 2). As ν_{TOT} values of zeolites are known to increase linearly with decreasing the atom fraction of Al in the zeolite framework,²⁰ this means that practically no framework dealumination occurs in the first minutes of acid treatment, hence that essentially extraframework Al species are extracted from the zeolite. The small decrease in the concentration of Brønsted sites (Fig. 2) could be due to a limited framework dealumination with elimination of bridging OH

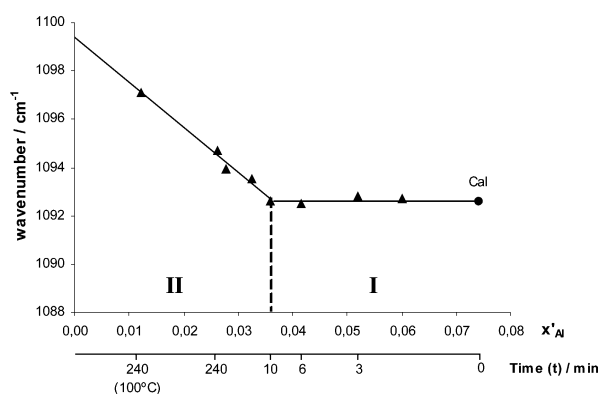


Fig. 1 Frequency vs. x'_{Al} , the atom fraction of Al in the HBEA samples. The duration of the acid treatment (*t*, in min) is also indicated on the abscissa.

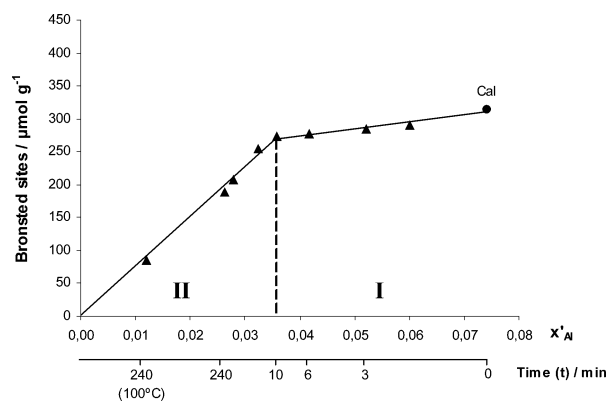


Fig. 2 Concentration of Brønsted acid sites vs. x'_{Al} , the atom fraction of Al in the HBEA samples. The duration of the acid treatment (*t*, in min) is also indicated on the abscissa.

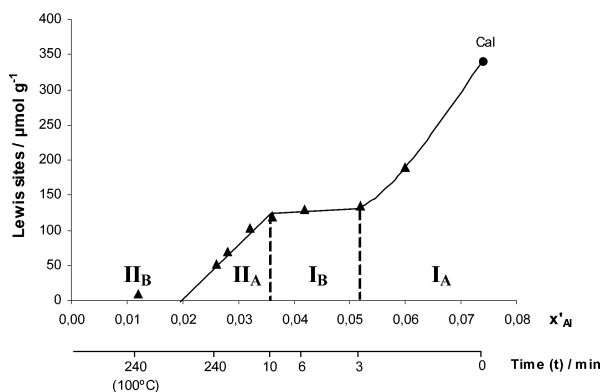


Fig. 3 Concentration of Lewis acid sites vs. x'_{Al} , the atom fraction of Al in the HBEA samples. The duration of the acid treatment (t , in min) is also indicated on the abscissa.

groups or/and to the extraction of extraframework Al species with Brønsted acidity, for instance of silica alumina debris.²¹

For $x'_{Al} < 0.036$ (Domain 2) *i.e.* for high t values, a linear correlation can be observed between v_{TOT} and x'_{Al} (Fig. 1). This suggests that no EFAL species are present in the zeolite (hence x'_{Al} is equal to the atom fraction in the zeolite framework), the increase in v_{TOT} being due to extraction of Al atoms from the zeolite framework. In agreement with this proposal, the concentration of protonic sites able to retain pyridine adsorbed at 150 °C is proportional to x'_{Al} (Fig. 2). This clear division into two domains is confirmed by the total disappearance of the band at 3660 cm^{-1} (ascribed to EFAL species) when x'_{Al} decreases from 0.074 to 0.036, by a maximum in the intensities of the bridging OH band at 3610 cm^{-1} and by the shift of the more intense XRD peak (302) towards higher 2θ values which is very pronounced for $x'_{Al} < 0.036$. Such a shift is characteristic of a framework dealumination.^{22,23}

Fig. 3 is more complex than Figs. 1 and 2. Both domains 1 and 2 can be divided in two parts: In domain 1 which corresponds to the extraction of EFAL species, there is at very short t values (≤ 3 minutes) *i.e.* for $0.052 \leq x'_{Al} \leq 0.074$ (I_A, Fig. 3), elimination of 60% of the Lewis sites. The number of Lewis sites eliminated 206 $\mu mol g^{-1}$ is only 1.5 times lower than the number of extracted Al atoms calculated from the x'_{Al} values. This means that most of the EFAL species eliminated at short t values are monomeric or dimeric. In contrast for 3 min $< t \leq 10$ min *i.e.* $0.036 \leq x'_{Al} \leq 0.052$ (I_B), there is only elimination of a small amount of Lewis sites (15 $\mu mol g^{-1}$) whereas there is extraction of 250 $\mu mol g^{-1}$ of EFAL. Therefore the EFAL species which are extracted are polymeric with a very low Lewis acidity per Al atom. Domain 2 corresponds to HBEA samples which do not contain any EFAL species. In consequence, the Lewis acidity of these samples can only be related to partially coordinated Al atoms (structure defects). The concentration of these defects on the Cal sample can be estimated to be equal to the concentration of Lewis acid sites of the acid treated sample with $x'_{Al} = 0.036$ *i.e.* to 120 $\mu mol g^{-1}$. When x'_{Al} decreases from 0.036 to 0.020 (II_A) there is a linear decrease of the Lewis acid site concentration with x'_{Al} . This indicates an extraction of the partially coordinated Al atoms. For $x'_{Al} \leq 0.020$ (extrapolated value in Fig. 3, II_B) the treated samples have practically no Lewis acid sites hence do not contain structure defects.

The rates of dissolution of the various Al species are different. Mono and dimeric EFAL species are extracted fast (8 mmol h⁻¹ g⁻¹),

polymeric EFAL species at least 4 times more slowly. The rate of dissolution of FAL species (corresponding to bridging OH groups and to framework defects) is much lower: 0.1 mmol h⁻¹ g⁻¹, moreover, there is apparently no difference in the rate of elimination of these two types of FAL species.

In summary, the characterization by pyridine adsorption of the Lewis and Brønsted acidity of samples resulting from acid treatment of calcined (or steamed) BEA samples allows a quantitative estimation of the various existing Al species. Thus, the HBEA sample characterized in this work was shown to contain approximately 300 $\mu mol g^{-1}$ of monomeric and dimeric EFAL species, 250 $\mu mol g^{-1}$ of polymeric EFAL species, 120 $\mu mol g^{-1}$ of partially coordinated Al atoms (structure defects) and 440 $\mu mol g^{-1}$ of Al atoms corresponding to bridging OH groups. Of course because of some oversimplifications such as the use of the same extinction coefficient for all the samples, this estimation is only semi-quantitative. However, this estimation of the concentration of the various Al species of HBEA zeolites should allow a better understanding of their catalytic properties.

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