Catalytic and acidic properties of boron pentasil zeolites

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Abstract – Pentasil-type zeolite with boron isomorphously substituted for
silicon in the pentasil zeolite framework and aluminum pentasil (ZSM-5
type) zeolite impregnated with a boron compound have been prepared and
studied. Lattice boron is shown to present trigonal or tetrahedral
environment depending upon ligand adsorbates and to induce a weak acid
strength and subsequently negligible catalytic activity for acidic-type
reactions such as methanol conversion to hydrocarbons, toluene alkylation
with methanol and toluene disproportionation. Some activity was observed
only if lattice aluminum was present or if aluminum based binder was
used. Lattice boron was shown not to modify appreciably shape selectivity.
Boron compound impregnated on aluminum pentasil sample was shown to
decrease the acidity and subsequently the catalytic activity for acid type
reactions but to sharply enhance shape selectivity, i.e. the yield in the
less bulky para isomers of aromatics with respect to the other isomers.
Boron of the impregnated compound (H_3BO_3) was shown to partly
isomorphously substitute for Si or Al upon calcination at 773 K while
calcination at 1073 K results in the partial formation of a glassy
borosilicate compound at the surface of the zeolite particles. These
findings are discussed in light of binder-zeolite interactions.

INTRODUCTION

Isomorphous substitution of elements such as B, Be, Ga, Cr, Fe, V, Ti, Ce, Zr, P... for
silicon and aluminum in zeolitic frameworks has largely been studied or claimed in the open
or patent literature (ref. 1-7). It was expected that acidic and porous properties of
zeolites may be modified by incorporation of elements of different size and different
chemical features. At the present time only boron seems to have resulted in actual industrial
applications for pentasil type zeolite materials in the Assoreni (methyl tert-butyl-ether
into methanol and isobutene) and Amoco processes (xylene isomerization and ethylbenzene
conversion) (ref. 3,8,9). Because of its small size and chemical features, boron was expected
to result in smaller unit cell volume and in new acidic properties when it takes the place of
aluminum. Many works have already been devoted to boron incorporation at lattice position in
the pentasil framework. Syntheses were performed using recipes (ref. 2,8) either derived from
that of Argauer and Landolt for ZSM-5 type material or in an ammonium fluoride medium
(ref. 10). Boron was claimed to be incorporated in the framework as a tetrahedral atom based
on data from X-ray diffraction (shrinkage of the unit cell) (ref. 2,3,11,12,13), infra-red,
ion exchange properties and NMR (ref. 3,5,11,14,15). Acidity induced by lattice boron was
shown to be much weaker than that due to lattice aluminum on the basis of thermoprogrammed
desorption of ammonia (TPDA) and proton NMR (ref. 16). Controversy still exists about
catalytic properties of boron pentasil zeolites. Negligible activity of pure boron pentasil
samples for acidic type reactions was reported (ref. 14,17,18) while activity was claimed for
pure silicon pentasil samples admixed with an alumina based binder (ref. 9,19,20).

The purpose of this invited paper is to bring some insight about the role of boron on acidic
and catalytic properties of pentasil-type zeolites. Boron could be incorporated into the
framework either during synthesis in the presence of a boron compound (ref. 2,8),
incidentally from pyrex (ref. 5) or after synthesis by solid-solid reaction or by having BCl_3
vapor contacting the sample (ref. 21). Several questions arise immediately : what new
properties are appearing due to the presence of lattice boron ? How can one unambiguously
prove that boron is into the framework and not occluded within the channels ? What is the
stability of lattice boron under catalytic reaction conditions, particularly when the zeolite
is admixed with an alumina based binder ?

EXPERIMENTAL

1. Preparation of samples

A large part of the samples were prepared in the laboratory of Professor R.Wey in Mulhouse, France following a procedure in an ammonium fluoride medium and with TPABr as a template agent (ref. 10), at a pH near 7. The ammonium form obtained was decomposed to get directly the acid form. Pure silica source was used while the autoclave was teflon lined to avoid impurity stemming from the vessel. H_3BO_3 or pure alumina were used as boron or aluminum source.

The impregnated samples were prepared as described previously (ref. 22) by impregnating an aluminum pentasil sample with H_3BO_3 aqueous solution, eliminating the excess solution by filtration and drying and further calcinating the samples at 773 K over-night. 0.3, 0.6 and 1.6 wt % boron impregnated samples were prepared.

2. Characterization

Chemical formulae were calculated from the chemical analysis of Na, Al and B. Crystallinity was determined by X-ray diffraction, infrared spectroscopy (vibration bands at ca 560 and 455 cm^{-1}) and n-hexane and 3-methylpentane (3 MePe) adsorption capacities. IR spectra were recorded with a Perkin Elmer 580 spectrometer on wafers prepared either by dilution in KBr (0.25 %) or as self-supported very thin pellets (2 to 4 $mg.cm^{-2}$). n-hexane adsorption capacity was determined at room temperature using a Sartorius microbalance after outgassing the samples at 723 K. X-ray diffraction was primarily performed by B. Mentzen (ref. 23) at the UCB, Lyon I using a home made step by step accessory. The morphology of the zeolite particles was characterized by a Cameca scanning electron microscope at the UCB, Lyon I.

Acidity was determined both by IR spectroscopy and thermoprogrammed desorption of ammonia (TPDA). In the former case hydroxyl group bands in the 3500-3800 cm^{-1} region were recorded on self-supported wafers after outgassing the samples at 723 K under $2x10^{-3}$ Pa pressure. TPDA experiments were performed by measuring by gas chromatography the amount of NH_3 desorbed upon heating ammoniated samples at a rate of 5 $K min^{-1}$.

RESULTS AND DISCUSSION

1. Infra-red data

The mid infra-red spectra for all samples are characteristic of the pentasil family with mean absorptions near 1230, 1100, 800, 560 and 455 cm^{-1}. The 560 : 455 cm^{-1} optical density ratio depends on the degree of crystallization with a maximum value near 0.62 (ref. 24) for calcined samples and 0.8 for as synthesized ones. The 1100 cm^{-1} band was observed to shift towards higher frequency when the Si/M ratio increased (M=B or Al) (Table 1, column 4).

TABLE 1. Some characteristics of B, Al and Si calcined samples

Samples	B per u.c.	Al per u.c.	Si-O vibration (cm^{-1})	o.d.560 / o.d.455 ratios	Particle size (μm)	adsorption capacity (wt %) n hex	3 MePe
A	1.25	0.28	1101	0.62	100x15x12	11.0	6.4
B	3.43	0.02	1099	0.57	50x25x20	–	6.7
C*	5.42	0.55	1093	0.46	2.5x1x0.4	8	4.7
D	0.08	4.08	1101	0.60	0.5x1x1	12	–
E	0.03	3.11	1098	0.60	0.6x0.6x1	13	9
F	0.01	3.61	1098	0.59	65x30x20	12	7.6
G	0.03	4.80	1100	0.60	30x12x8	11	7.4
H	–	0.06	1102	0.60	560x80x80	–	–
I	–	0.11	1120-1083	0.57	5x0.7x1	12	8.8

* crystallinity measured by XRD was only equal to 72% against 100% for all the other samples.

Differences between B- and Al- pentasil zeolite spectra were better seen for self-supported thin wafers rather than for KBr pellet. Moreover, effect of adsorbates on peak intensity could also be studied. The difficulty was to prepare wafers thin enough to allow one
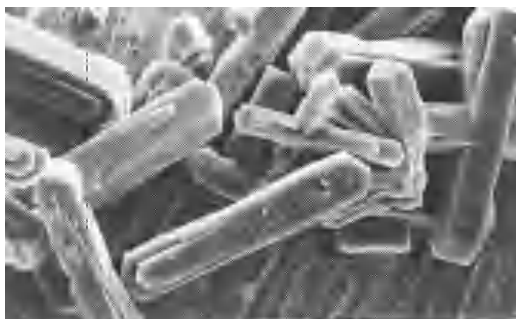
Fig. 1. SEM photograph of sample A. 1 cm = 25 μm.

infra-red beam transmission at a convenient level for precise analysis. It was then observed that the boron pentasil samples exhibited additional bands near 1380, 920, 700 and 670 cm^{-1} and a small shoulder near 970 cm^{-1} (Fig. 2). The strongest band at 1380 cm^{-1} is one to two orders of magnitude smaller than the band at 1100 cm^{-1} which makes it difficult to evidence clearly. The assignment of the different bands is based on previous data on borates and borosilicate glasses or films. (ref. 25-27).
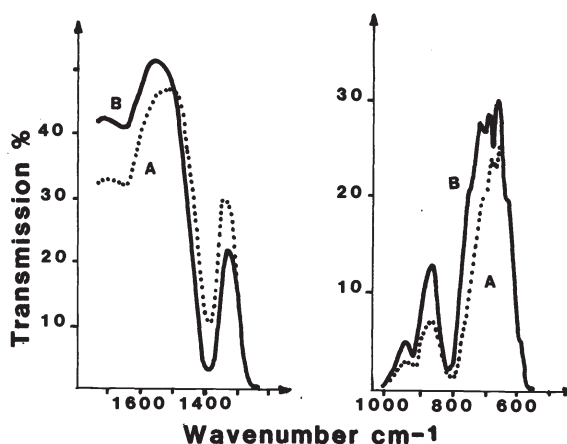

Fig. 2. IR spectrum of self-supported wafers of samples A and B calcined.

Boron in 3-fold coordination is characterized by the presence of a very strong absorption in the 1100-1400 cm^{-1} range due to the B-O asymmetric stretching vibration (ref. 25). The frequency of this band depends on the B-O bond order i.e. on the nature of the next neighbours and shifts from 1265 cm^{-1} for B_2O_3 (B^{3+} next neighbours) to 1380 cm^{-1} for borosilicates (Si^{4+} next neighbours) (ref. 26,27). Moreover, in borosilicates bands at 920 cm^{-1} and 670 cm^{-1} were observed and attributed to the symmetric stretching and out-of-plane bending B-O-Si modes.

It may be concluded that in the calcined forms of the boron pentasil samples, the ion B^{3+} is located near three O^{2-} bound to Si^{4+}, i.e. near a trigonal face of a tetrahedral framework site.

When ammonia, methanol or to a lesser extent water was adsorbed on the 673 K outgassed boron pentasil samples the bands at 1380, 920, 700 and 670 cm^{-1} were observed to decrease in intensity while a new band of much lower intensity developed at 1470 cm^{-1}. This behaviour was reversible upon outgassing at room temperature. Such a behaviour was already mentionned by Taft (ref. 28) by hydration of borosilicate films and was interpreted as due to the formation of B(OH) species.

The triply degenerate stretching mode of BO_4 groups is expected near 1090 cm^{-1} and was indeed observed at 1130 and 926 cm^{-1} due to a degeneracy removal for danburite, a calcium borosilicate and at 1170 and 1090 cm^{-1} for BPO_4, where boron is tetrahedrally coordinated in both cases. In boron pentasil samples it seems

difficult to evidence tetrafold coordination of boron since the main peaks are
masked by the intense Si-O vibration. The reversible variations of IR spectra upon
adsorption of NH_3, CH_3OH or H_2O may be tentatively explained as follows : due to
its small size boron ion locates near three oxygens in a trigonal environment but
in a tetrahedral hole of the pentasil framework in a configuration described by
Scholle et al. (ref. 16). One then gets BO_3-type vibrational modes for dehydrated
samples. Upon adsorption tetrahedral coordination is easily obtained.

Scholle et al. (ref. 16) also observed a reversible change in the MAS-NMR spectra of [11]B upon
dehydration of boron pentasil samples and interpreted this phenomenon as due to a
transformation of tetrahedral to trigonal boron and vice versa.

In order words one may conclude that boron at lattice position presents either
trigonal or tetrahedral symmetry depending on the absence or presence of
adsorbates. The main peaks are at ca 1380, 920, 700 and 670 cm^{-1} for such trigonal
boron but unfortunately, tetrahedral boron is not detectable in pentasil zeolites.

2. X-ray diffraction analysis

Changes in the unit cell dimensions of a zeolite material as a function of Si substitution by
elements such as Al are well documented and may be very useful to characterize such a
substitution. It was previously shown that the unit cell size increased when the amount of Al
in the framework increased in Y-type (ref. 29) or in ZSM-5 type zeolite. In contrast
substitution of Si by boron in pentasil-type zeolite resulted in unit-cell contraction
(ref. 2,13). These features are correlated to shorter B-O and longer Al-O bond lengths (1.39
and 1.67 Å respectively) compared to that of Si-O (1.61 Å). Calculation of the unit cell
volume necessitates a least squares refinement. An easier way to characterize the variations
of the unit cell size is to follow the changes of the sum (ΣT) of four peaks between 2Θ =45
and 48° since it represents the magnitude of a general reciprocal lattice vector. Peaks
correspond to four d spacings 10,0,0/4,9,1-0,10,0/1,8,4-4,3,6 and 9,3,3 (ref. 13,23,30).

Experimental data from our own and from literature are given in Fig. 3 and 4. It turns out
that for pentasil type zeolites Al content does not modify the unit cell appreciably in the
Al content range studied while boron results in an appreciable unit cell shrinkage. Such a
plot may inversely be used to determine if boron is really incorporated into the lattice or
not, as far as one can be confident in the standardisation. The agreement between different
research laboratories led us to reasonably trust the validity of the curve.

It is interesting to determine the effect of boron impregnation on the unit cell volume. The
ΣT values for boron impregnated Al pentasil zeolite samples are shown in Fig. 4 by an arrow.
It clearly appears that part of boron has been incorporated into the zeolite framework (Note
that the crystallinity decreased for high boron content) : 1.6 and 2.7 B/u.c. for 0.3
(= 1.6 B/u.c.) and 1.6 (= 8.5 B/u.c.) wt % samples.

In order to support this finding a MAS-NMR study of hydrated samples has been carried out in
Namur by J.B.Nagy. [11]B spectra clearly showed (ref. 22) that boron was incorporated in the
framework (δ=-3 ppm) but the quantitative determination of boron content was unprecise. The
MAS-NMR spectra of [29]Si could be used for determining if Al was eliminated from the lattice
from Si-(0) Al peak. Accuracy was unfortunately not good enough to be really conclusive
although the experimental values tend in the right direction.

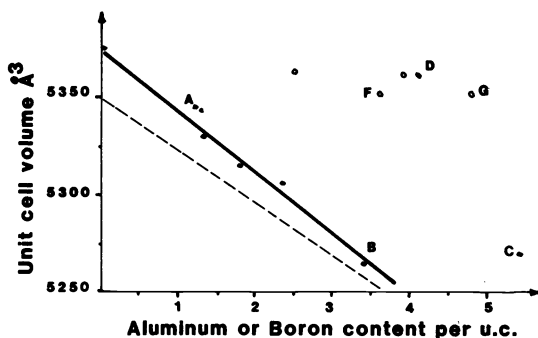Fig. 3   Fig. 4

Fig. 3. Variations of unit cell volumes with B and Al contents.
Position for sample C out of the curve indicates that part of
boron is not in the lattice. The dashed curve stems from ref. 3
and the not labelled dots correspond to other samples of our
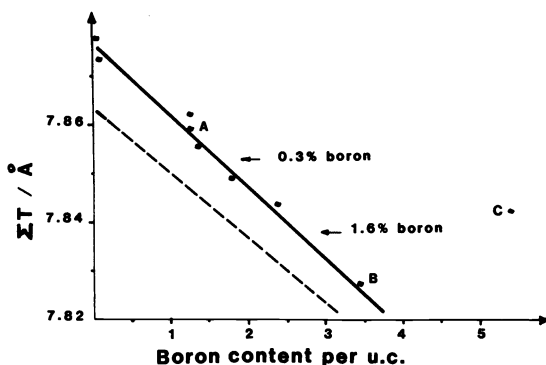own not described in this paper.

Fig. 4. Variations of the sum ΣT of the four XRD peaks at 2Θ = 45 to 48°

3. Characterization of acidity

Acidity can be measured in a variety of ways (ref. 31). For pentasil type materials the basic probe should be of size small enough for it to enter the zeolite channels which excludes the Hammett type indicators technique. Infra-red spectroscopy of hydroxyl groups and of NH_3 adsorption and thermoprogrammed desorption of adsorbed NH_3 turn out to be the most reliable techniques. Experimental results shown in Fig. 5 and 6 and Table 2 are consistent with previous works (ref. 16,21,32,33,34). Some striking features can be summarized as follows :

Framework Al results in strong acidity with the corresponding hydroxyl group band at ca 3605 cm^{-1} (ref. 35) and two TPD peaks at 500 K and 710 K.
Framework B results in weak acidity with a broad IR OH band at ca 3700 cm^{-1} and a TPD peak at ca 465 K.
Framework terminal Si results in very weak acidity with the IR OH band at ca 3740 cm^{-1} and a very weak TPD peak at ca 380 K.

The acidity strength may be schematized as :

$$Si < B \ll Al$$

It is interesting to compare the number of NH_3 desorbed in TPD experiments as a function of B or Al content as shown in Table 2. As usually observed the experimental values are lower than those determined from chemical formulae. As TPD measurements started at 373 K to avoid weakly chemisorbed and physisorbed NH_3, the data show that weak acid sites exist for B and Al pentasil zeolites.

Note that a broad band near 3520 cm^{-1} was observed for some of our boron-pentasil sample. Such a band was already mentionned for aluminum-pentasil samples (ref. 6). It may be assigned to special defects involving gem type hydroxyls $T < ^{OH}_{OH}$ (T=B, Al or Si).

For impregnated samples the 3605 cm^{-1} band intensity was observed to decrease with boron content (ref. 22) while a band near 3700 cm^{-1} developed. This shows that impregnation with boron decreased the zeolite acidity and created new hydroxyl group similar to those of boron
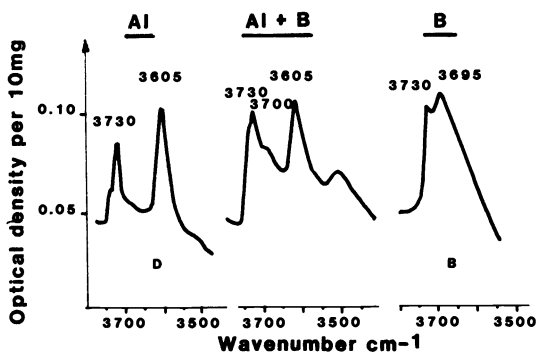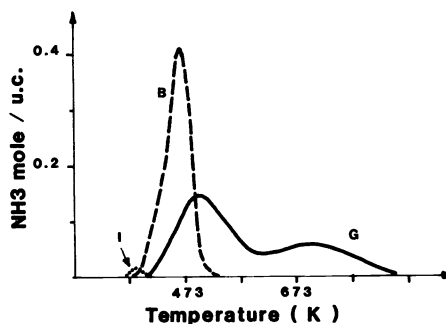

Fig. 5

Fig. 6

Fig. 5. IR spectra of self-supported wafers outgassed at 723 K for samples B and D and for Al, B- pentasil sample (Al=1.5/u.c. and B=0.4/u.c.) (central spectrum).

Fig. 6. Plots of thermoprogrammed desorption of NH_3 versus temperature above 373 K. Samples B, G and I were outgassed at 723 K under oxygen flow and saturated with NH_3 at 373 K.

TABLE 2. Thermoprogrammed desorption of ammonia of several samples outgassed at 723 K, NH_3 being adsorbed further at 373 K

Samples	M/u.c.	Total acidity (mol/u.c.)	Strong acidity (mol/u.c.)
B	3.4 B	2.5	0
G	4.8 Al	1.7	1.2
I	0.1 Al	0.04	0

[a] amount of NH_3 desorbed between 373 and 873 K, rate 5 K min^{-1}
[b] amount of NH_3 desorbed between 600 and 873 K, rate 5 K min^{-1}.

pentasil. Microcalorimetry measurements of NH_3 adsorption showed (ref. 22) that strong acid sites are still present in lower concentration and that the overall acidity decreased with boron content. These findings are coherent with both neutralisation of acid OH groups by boron as for phosphorous (ref. 36) and substitution of (Al,Si) by B.

If impregnated samples were calcined at 1073 K their acidity was observed to decrease while XRD patterns showed a loss in crystallinity particularly for the high boron content and T values returning to its starting value for not impregnated samples. Moreover, MAS-NMR spectra (ref. 22) present a peculiar feature as observed in particular recording conditions ($\Theta = 36°$) for borosilicates (ref. 37). It is very probable that boron compound reacted with the zeolite at the solid-solid interface resulting in a borosilicate glassy compound.

4. Catalytic properties

All samples were studied in three different acid type reactions, namely methanol conversion (WHSV = 5 h^{-1}, T = 623 K), toluene alkylation with methanol (WHSV = 5 h^{-1}, T = 653 K) and toluene disproportionation (WHSV = 0.5 h^{-1}, T = 753 K).

The results can be summarized as follows. Lattice boron has no catalytic activity in our conditions. Methanol was only converted to dimethyl ether and low olefins at 873 K but life time was very small and autocatalytic feature was not observed. Some catalytic activity was observed when some lattice aluminum was present. In presence of both lattice Al and B, activity follows the amount of Al while selectivity particularly for para-xylene was not appreciably modified with respect to pure Al pentasil sample. Selectivity in para-xylene was observed to depend, greatly on the particle size. For instance, 55% para-xylene was obtained in toluene alkylation with methanol for particle size in the range 1 to 2 μm and reached more than 90% for particles of several hundreds μm.

For impregnated samples selectivity in para-xylene was observed to increase with the amount of boron. In the first minutes, one goes from 55% for standard Al pentasil zeolite, to 58% for 0.3 wt% B, 70% for 0.6 wt% B and 88% for 1.6 wt% B.
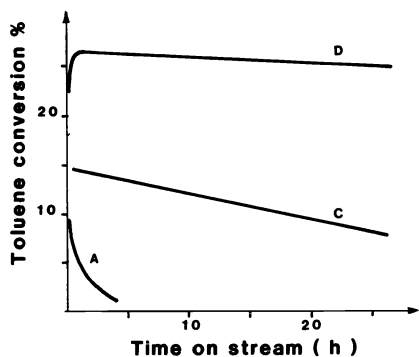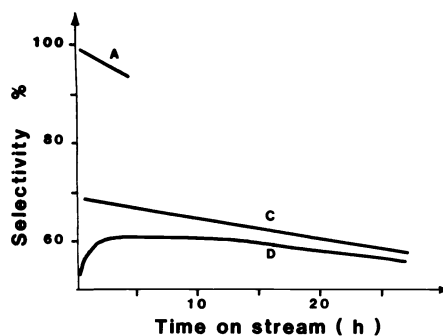

Fig. 7   Fig. 8

Fig. 7. Variations of activity for toluene alkylation at 673 K versus time on stream for samples A, D and G. Tol.:$CH_3OH=4:1$.

Fig. 8. Variations of selectivity for para-xylene for reaction and samples as in Fig. 7.

XRD and NMR studies have shown that part of B was substituted for Si,Al in the framework particularly for low B content while for high boron content, amorphous phase was developed. This result supports the catalytic behaviour since extraframework boron amorphous phase creates additional hindrance to reactants and product diffusion.

CONCLUSIONS

The main conclusion which may be drawn from this work and from previous findings is that boron may be incorporated into pentasil framework by isomorphous substitution of lattice silicon atoms. Due to its small size and its chemical features boron occupies a tetrahedral site but may undergo a trigonal environment in the absence of adsorbates. The incorporation of boron in the framework may be easily followed by XRD since shrinkage of u.c. volume occurs.

Lattice boron creates a weak acidity closer to the very weak acidity of pure silicon pentasil than to that of aluminum pentasil as shown by IR (band at ca 3700 cm^{-1} against 3605 cm^{-1}) and TPDA. This acidity does not play any detectable role in catalytic activity for acid type reactions such as methanol conversion, toluene alkylation with methanol or toluene disproportionation.

Impregnation of aluminum pentasil sample with H_3BO_3 and its further calcination at 773 K results in partial substitution of lattice Si,Al by boron and therefore to a decrease in acidity and in catalytic activity. Excess of boron creates additional constraint to diffusion and subsequently enhances shape selectivity. Calcination at 1073 K creates glassy borosilicate at the surface of the particles and some loss in crystallinity due to reaction between the zeolite and the boron oxide. This feature together with the change in symmetry environment of lattice boron upon adsorption of adsorbates such as CH_3OH, NH_3 or H_2O indicate that some mobility of boron may be expected during catalytic reaction.

Previous works on the effect of alumina based binders to boron or pure silicon pentasil zeolites have shown that catalytic activity may be created by the interaction of the binder with the zeolite during thermal treatment or during catalysis. Incorporation of Al into the framework may well have occurred although occluded aluminum hydroxy compounds may play an important role. In the present case a low melting point oxide such as B_2O_3 clearly reacts with the zeolite matrix involving boron substitution for Si and Al and even partial loss in crystallinity. It is obviously not possible to simply extrapolate to other binders such as alumina which are more stable. The IR hydroxyl bands, MAS-NMR of [11]B and the XRD peaks position are certainly the best features to follow to determine the amount of lattice boron in the sample.

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