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Si,Al Ordering and Basicity Clusters in Faujasites[†]

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The basicity of cation exchange faujasites is described in terms of basicity clusters. Those clusters are based on both the Al location in the framework and the faujasite topology. They are built from an aluminum taken as origin (Al_0) surrounded by neighboring layers (0−3) of TO_4 tetrahedra where an inductive influence of Al is effective through the framework. These clusters allow for the calculation of the basic strength and of the estimated number of basic sites. The framework oxygens are stronger, for the strong or the global basicity, when they link an Al atom in a layer *n* to two Si in the layer *n* − 1 of the cluster. This is the basis of a framework-induced basicity. It follows that in X, Y, or dealuminated Y various schemes show how much the Si,Al ordering plays a major role in the basicity. A combination of the different possible clusters in a crystal is suggested to take into account the experimental evidence of a range of basic strengths. On average, X zeolite not only contains more and stronger sites than Y but it also shows the highest ratio of strong to global basicity. The weak basicity of cationic dealuminated Y is connected through the clusters to its strong acidity in the protonic form. The clusters, more generally called topological clusters, may be applied to the case of properties other than basicity (like the redox behavior when transition metal cations are present) and to porous materials other than zeolites.

Introduction

The interest in basic materials and particularly basic zeolites has grown considerably in the past years. They are used in catalysis[1−5] and in separations by adsorption.[2,6,7] The intrinsic (or structural) basicity linked to the framework oxygens of a zeolite may be modified by extraframework species (various oxides, grafted groups or molecules, metals aggregates, ...)[2] forming an extrinsic basicity. A better knowledge of the two forms of basicity has to be reached in order to understand the behavior of such basic catalysts and sorbents. In the first step the intrinsic basicity is considered. The negative charges born by the framework oxygens originate from the presence of AlO_4 tetrahedra, and the distribution of charges strongly depends on the compensating cations.[8] An average basic strength may be defined, and simultaneously a range of basic strengths is generated by the Al content and the cations.[2,8−11] This is evidenced, for instance, by the pyrrole adsorption on various zeolites.[12,13] The basicity also depends on the type of framework oxygen (O1 to O4) in faujasite, acting as a basic center.[8]

The question then arises as to what extent the framework itself may induce some specific basicity. In this view a recent approach considers the chemical environment of AlO_4 tetrahedra, which are the species creating the basicity,[14] by looking at the $Al_0O(SiO)_aAlO$ sequences around any given framework aluminum (Al_0) taken as origin. The variable *a* represents the number of SiO intercalated between two AlO, i.e., the topological distance between them (1, 2, 3, ...). For *a* = 1 the oxygen basicity is strong because of the closeness of Al atoms, and for

a = 2 it is medium or weak. At higher *a* values the Al atoms are too far for an inductive effect through the framework to be effective. Around this Al_0 atom all the $Al_0O(SiO)_aAlO$ sequences form a pseudospherical volume that contains all the basic oxygens of a framework. The strong basicity cluster for *a* = 1 comprises all the stronger oxygens. The global basicity cluster for *a* = 2 brings together all the basic oxygens, strong, medium, and weak. It follows that the number of TO bonds between the central Al_0 and the other Al considered is 2 for strong basicity and 3 for global basicity. It turns out that the topology of each framework determines the connection of the TO_4 tetrahedra and the number of T sites in each layer around a central Al_0 atom. For instance, beyond the four Si of the first layer, the second layer of T sites consists of 9−12 atoms in the usual zeolites. It follows that these T sites are not connected in the same way in the different zeolites. In faujasite, for instance, three of the nine atoms of the second layer are connected twice to the Si of the first shell, forming 4MR apertures. The basicity introduced by an Al in such a doubly bonded site creates half a charge instead of one-quarter for an Al singly bonded to the Si layer. This gives rise to a framework-induced basicity that is characteristic of each zeolite.[14] The present study considers in detail the case of faujasite clusters, with regard to the topology[15] and to the Si,Al ordering proposed from ^{29}Si MAS NMR[16−20] or crystallographic studies.[21]

Faujasite Framework and Basicity

Figure 1 shows the T sites around a central atom numbered 0. All the faujasite sites have the same topology with four Si in the first layer (atoms 1−4) and Al or Si in the second layer (9 atoms, 5−13). The third shell (16 atoms, 14−29) contains Si
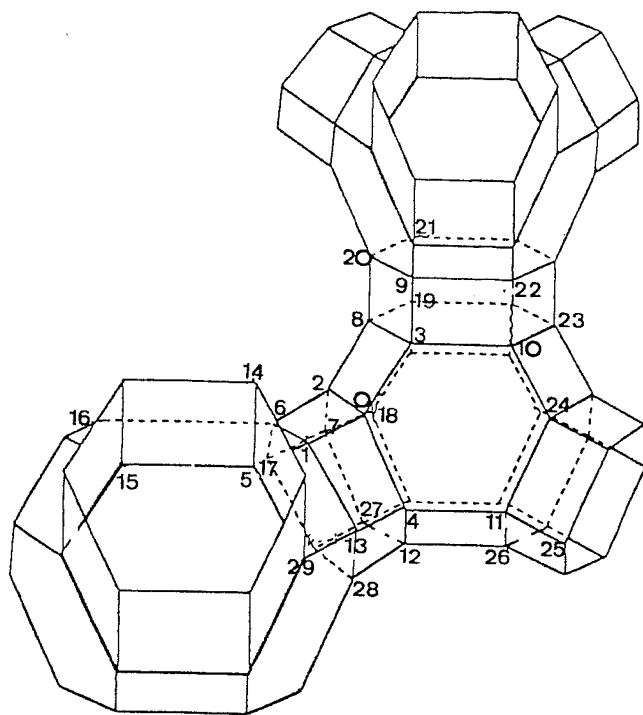

Figure 1. Framework of faujasite showing a central T_0 site surrounded by 4 first neighbors (1−4), 9 second neighbors (5−13), and 16 third neighbors (14−29). (Reprinted with permission from ref 27. Copyright 1991 Elsevier.)

or Al, taking into account the Lowenstein rule. It may be noted that the faujasite framework shows a high interconnectivity of T sites, while for instance ferrerite has 12 atoms in the second shell and 21−27 in the third one depending on which T site type is considered. These differences in atom arrangements are expressed by a topological density TD_i which is the ratio of the actual number of TO_4 in layers $0-i$, given in ref 15, to the maximum numbers (12 and 36) in layers 2 and 3. The TD_2 and TD_3 values are respectively 0.82 and 0.57 for faujasite and 1 and 0.74 for ferrierite.[14] The other usual zeolites (L, β, mordenite, ZSM-5, ...) lie between these values. It was shown first that for a given number of T sites occupied by Al in the basicity clusters the less topologically dense zeolites, i.e., with fewer atoms in layers 2 and 3 like faujasite, give rise to a stronger basicity because of the fact that some Al atoms contribute more to the negative charge born by the oxygens. Second, the same given basic strength requires fewer T sites occupied by Al in the zeolites with a low topological density. It follows that the faujasite framework is a good candidate for generating strong basicity.[14] This is experimentally observed.[2,9]

With regard to the Al location in the framework, some information is already known. First, several Si,Al orderings are proposed as fitting the ^{29}Si NMR[16−19] and the crystallographic[21] studies. Second, a qualitative description of the models proposed is possible. For the X zeolite, most of the square faces contain two Al with one Al in a few cases, and there are usually three and less often two Al in the hexagonal face accessible from the supercage.[16−19] This means that there may be around eight Al in the nine T sites 5−13 of Figure 1. In Y, the hexagonal face may contain two Al either in the para or in the meta location. None contains three Al, and some may exhibit only one Al. The 4MR apertures of sodalite may contain one or two Al. It follows that site 8, which belongs to this cage, may or may not be occupied by Al. The square faces of the hexagonal prism may contain one Al (atom 0) or two Al (0 and 6 or 13), and there are no adjacent faces containing two Al (0 and 6 and 13).
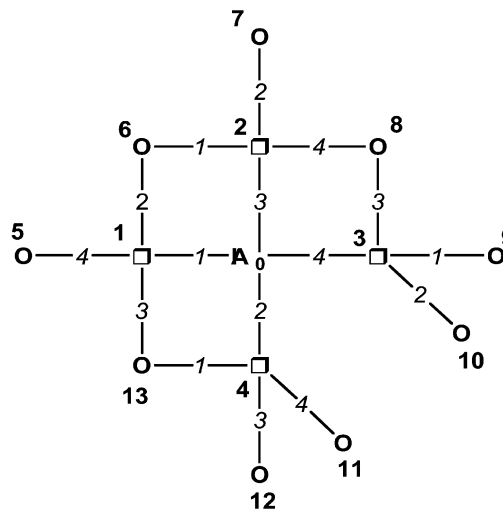

Figure 2. Strong basicity cluster in faujasite: (Al$_0$) central Al; (○) Al or Si; (□) Si. The bold numbers correspond to the T sites of Figure 1. The italic numbers are the O1, O2, O3, and O4 oxygens of the TOT bonds.

As already indicated above, the distribution of charges is modified by the compensating cations for a zeolite material characterized by a given Al content. In faujasite the cation site I is located at the center of the hexagonal prism, sites II and II′ are centered on the hexagonal face of the sodalite cage, site II being in the supercage, and site III is in the supercage above square faces. The population of the cations at each site depends not only on the cation itself but also on the Al location and on external parameters such as the temperature or the presence or not of adsorbed phases.[12,13,22] The influence of the cation is related to several parameters such as its size, location content, and electronegativity.[2,8] An exchange of cations at the same site modifies the charges on the various oxygens.[8] It follows that the basic strength of the oxygens of any of the basicity clusters depends on their position with regard to Al and to cations.

In summary, it may be said that the aluminum atoms are the primary factors that create the basicity by the negative charges they introduce in the framework through the AlO$_4$ tetrahedra. This basicity is regulated by the cations, which attract more or less the negative charges, inside a basicity range defined by this Al content. In faujasites it is known that the cesium forms have the strongest basicity related to the weak electronegativity of the cation.[2,8,9] In what follows, mainly the influence of the Al parameter is considered in order to describe the detailed structural characteristics of the basicity of the oxygens. Two main points will be considered for the same cation, Na, for example: (i) the strength depending on the Al location and (ii) the number of sites evaluated from the number of Al in the cluster (T_{Al}) because it is impossible to know exactly to what extent some oxygens are more important for basicity and consequently to count them unambiguously.

Strong Basicity Cluster

Figure 2 depicts the strong basicity cluster. As easily seen, it is part of Figure 1. All the T sites in faujasite belong to one hexagonal face of the sodalite cage and to three square faces, one of the sodalite (sites 0, 2, 8, 3) and two of the hexagonal prism (sites 0, 4, 13, 1, 6, 2). The hexagonal window of the sodalite contains the atoms 11, 4, 0, 3, 10 and is not fully completed in this cluster. The four types of oxygens of the faujasite framework are localized in Figure 2. The O1 and O4 atoms belong to the 12R window. They were shown to be the

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TABLE 1: Characteristics of Possible Basicity Clusters in X (See Figures 3, 7, 8) and in Y Zeolites (See Figures 4, 9)

strong basicity				global basicity						
cluster	$T_{Al}{}^a$	$m_{Al}{}^b$	$x_S{}^c$	$-\delta_0{}^d$	cluster	$T_{Al}(s)^a$	$T_{Al}(mw)^e$	$s/g{}^f$	$m_{Al}{}^b$	$x_G{}^c$	$-\delta_0{}^d$
X_s-1	10	0.5	4	0.429	X_g-1	10	0	100	0.5	10	0.356
X_s-2	9	0.469	3.75	0.417	X_g-2	9	2	82	0.475	9.5	0.351
X_s-3	8	0.437	3.5	0.406	X_g-3	8	3	73	0.437	8.75	0.341
X_s-4	8	0.437	3.5	0.406	X_g-4	8	3	73	0.45	9	0.345
X_s-5	8	0.406	3.25	0.396	X_g-5	8	3	73	0.45	9	0.345
X_s-6	7	0.375	3	0.383	X_g-6	7	5	58	0.437	8.75	0.341
Y_s-1	5	0.31	2.5	0.358	Y_g-1	5	3	63	0.29	5.75	0.301
Y_s-2	5	0.29	2.25	0.345	Y_g-2	5	2	71	0.29	5.75	0.301
Y_s-3	4	0.29	2.25	0.345	Y_g-3	4	5	44	0.29	5.75	0.301
Y_s-4	4	0.25	2	0.332	Y_g-4	4	6	40	0.29	5.75	0.301
Y_s-5	4	0.25	2	0.332	Y_g-5	4	5	44	0.29	5.75	0.301

^{a} T_{Al} or $T_{Al}(s)$: number of T sites occupied by Al in the strong basicity cluster (second layer of tetrahedra). ^{b} m_{Al}: Al molar fraction in the cluster. ^{c} x_s or x_g: number of charges introduced in the cluster by Al for strong (s) or global (g) basicity. ^{d} $-\delta_0$: mean basic strength (Sanderson calculation). ^{e} $T_{Al}(mw)$: number of T sites occupied by Al generating medium and weak basicity (third layer of tetrahedra). ^{f} s/g: percentage of $T_{Al}(s)$ to $T_{Al}(s) + T_{Al}(g)$.

most basic oxygens of the faujasite.[8] The atoms O2 and O3, which are less basic, form the two six-rings of the hexagonal prism. One may observe that O1 and O4 are present in only one type of cage (6MR and sodalite, respectively) while O2 and O3 are shared between the two types. The T atoms of the second layer (6–13) are either singly bonded to the Si of the first layer (atoms 5, 7, 9, 10, 11, 12) or doubly bonded (6, 8, 13). The general formula of the cluster is $(Al_xSi_y)O_{16}Me_x$. Me is the metal cation, with $x + y = 8$, and the molar fraction is $m_{Al} = x/(x + y) \leq 0.5$. An Al atom counts for 1/4 of the charge of the cluster if it is singly bonded and for 1/2 in the doubly bonded case. Assuming, for instance, beyond a central Al in 0 (Al_0), that there is one Al in the second layer, the cluster formula is either $(Al_{1.25}Si_{6.75})O_{16}Me_{1.25}$ or $(Al_{1.5}SiO_{6.5})O_{16}Me_{1.5}$. In addition in the cluster considered, it is noted that because of the different basicities of O4 and O2, for instance, a singly bonded Al in site 5 or 7 does not contribute the same amount to the basic strength. One may speculate about the higher strength of oxygens O1 and O4, which, independently of any influence of bond lengths and bond angles, may eventually come from a specific location of Al in some T sites. In this paper no further study will concern this kind of basicity depending on the type of oxygens. The attention is mainly focused on the basicity clusters, whatever the oxygen type, related to the topology in the faujasite family, X, Y, and dealuminated Y.

In the X zeolite, Al may be located at the nine T sites of the second layer giving $m_{Al} = 0.5$. The corresponding strong basicity cluster denoted X_s-1 is represented in Figure 3. Its formula is $(Al_4Si_4)O_{16}Na_4$ for the sodium form, for instance. In fact, in the usual X zeolites m_{Al} is close to 0.45, which corresponds to 84–86 Al per unit cell. One may not expect to reach 0.45 for m_{Al} in a small cluster with only 14 atoms. As seen further, this value is obtained for the global basicity cluster. Nevertheless, for m_{Al} close to 0.45, the distribution of Al atoms may be suggested from models issued from studies by ^{29}Si NMR of Si,Al ordering. Some examples are given in Figure 3, which fit the NMR results mentionned above. Table 1 gives the main characteristics of these clusters. The formulas of the sodium clusters X_s-2 to X_s-6 vary from $(Al_{3.75}Si_{4.25})O_{16}Na_{3.75}$ to $(Al_3Si_5)O_{16}Na_3$. The average basic strength ($-\delta_0$), calculated using the Sanderson principle of equalization of electronegativities[23] and shown in Table 1 (0.417–0.383), is parallel to the changes in the x_s values (3.75–3). The number of T sites occupied by Al, an image of the number of basic sites, decreases in the series simultaneously with the amount of negative charges, x_s, from 9 to 7. Some other remarks may be made. In the clusters X_s-4
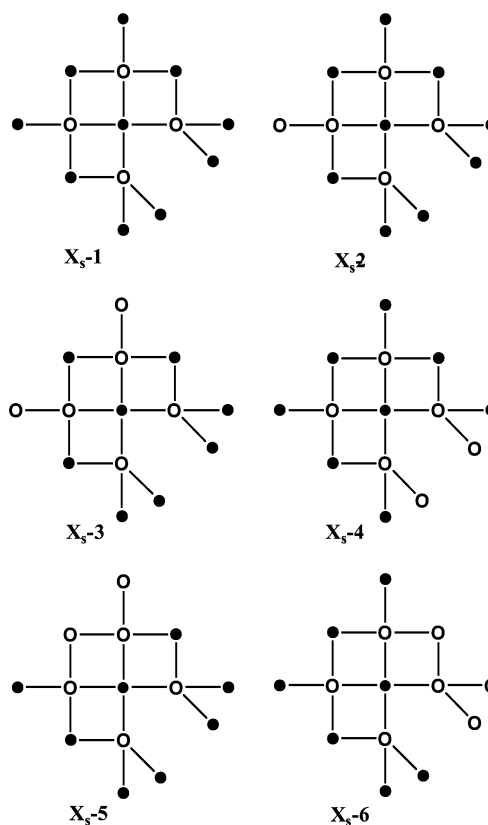
Figure 3. Some possible strong basicity clusters for X zeolite: (●) Al; (○) Si.

and X_s-6, the Al and Si locations prevent the presence of three Al in the hexagonal face of the sodalite. It is noted that the same number of T sites occupied by Al in the cluster may generate different basic strengths (X_s-5 versus X_s-3, X_s-4). A same number and strength of basic sites may involve a different meta or possible para location of Al in the sodalite hexagonal face (X_s-3 versus X_s-4). All these results show the importance for basicity of Al doubly or singly bonded to the Si layer. The possibility of having different strong basicity clusters suggests that a zeolite crystal may be constructed with a mixture of several types of clusters. Al distributions were already proposed from ^{29}Si NMR[16–19] and crystallographic studies.[21]

The case of Y zeolite opens a larger number of possibilities that may be restricted further in the global basicity cluster. A number of 56 Al per unit cell ($m_{Al} = 0.29$) suggests around four to five Al in the strong basicity cluster, i.e., three to four
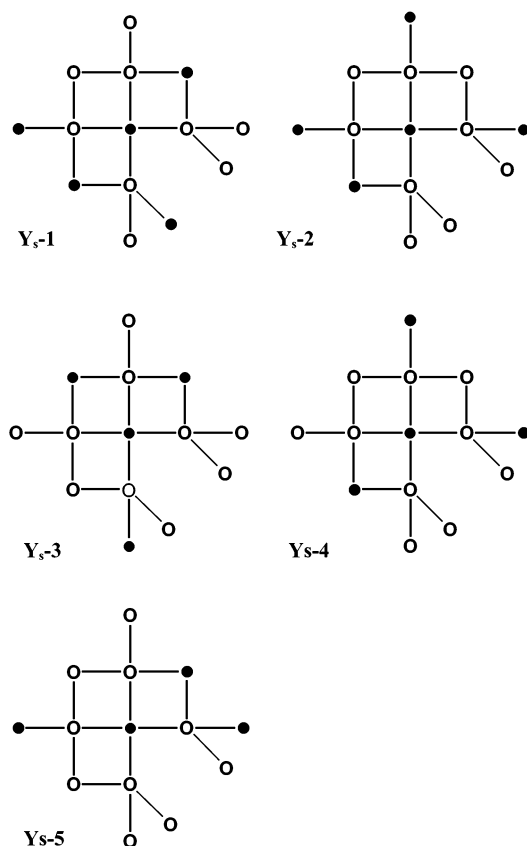
Figure 4. Some possible strong basicity clusters for Y zeolite: (●) Al; (○) Si.
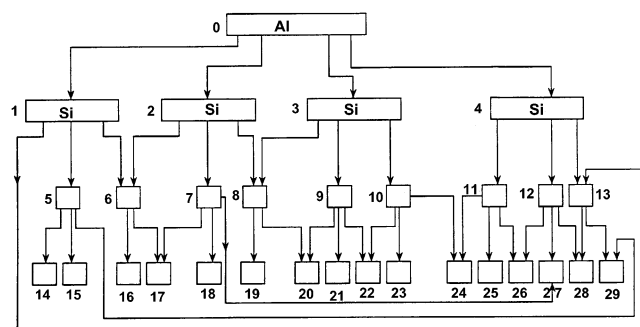

Figure 5. General scheme of the global basicity cluster in faujasite including strong, medium, and weak sites. It shows the interconnectivity of T sites, particularly the sites of one layer n being doubly or singly bonded to sites of a layer $n - 1$. The numbers corresponds to sites of Figures 1 and 6. The open squares are Si or Al. (Data are from ref 27.)
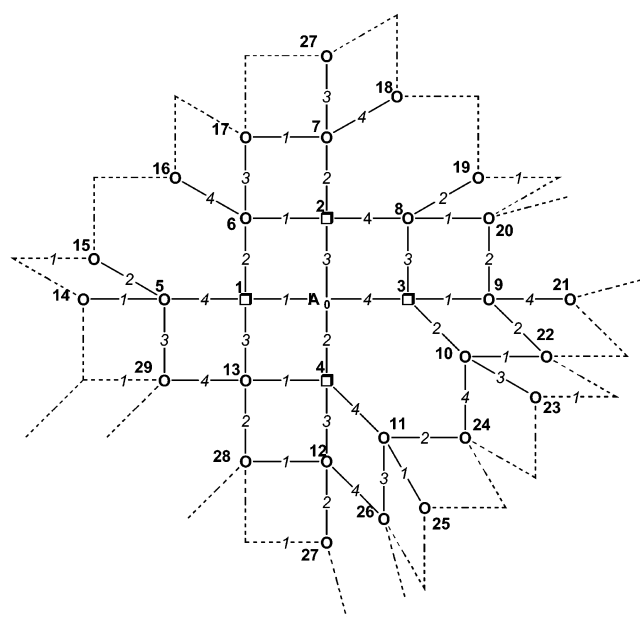

Figure 6. General scheme of the global basicity cluster in faujasite including strong, medium and weak sites: (Al_0) central Al; (□) Si; (○) Si or Al. The bold numbers correspond to the T sites of Figure 1. The italic numbers are the oxygens O1, O2, O3, and O4. The dashed lines do not belong to the cluster and suggest the contiguous apertures.

in the second layer around the central Al_0. The Al distribution has to leave open the location of Al in the third layer in order to follow the Lowenstein rule. The ^{29}Si NMR studies of Y suggested models[16−19] with the general conclusions reported above. In the strong basicity cluster only a part of the hexagonal face belongs to the cluster. Five examples of possible strong basicity clusters for Y, denoted Y_s-1 to Y_s-5, are given in Figure 4. Their formulas vary from $(Al_{2.5}Si_{5.5})O_{16}Na_{2.5}$ to $(Al_2Si_6)O_{16}$-Na_2. The basic strength decreases in the same order with the values of x_s and with the calculated average basicity $(-\delta_0)$ (Table 1). The number of T sites occupied by Al shows only a few changes in the series (from 5 to 4), but the Al location reflects again the importance of singly or doubly bonded Al. For instance a same m_{Al} and x_s (same basic strength) is seen for Y_s-2 and Y_s-3 while the number of Al sites (T_{Al}) involved is different. A same number of T sites filled with Al may give different m_{Al} and x_s (Y_s-1 versus Y_s-2 or Y_s-3 versus Y_s-4 and Y_s-5). The occupation of the hexagonal face of the sodalite involves Al in Y_s-1 only at one meta site, while the para case may exist in the four other clusters. As in the case of X zeolites, there may be a combination of various clusters in a crystal to reach the mean m_{Al} value of Y.

The removal of Al to obtain dealuminated zeolites is known to generate strong acidity in the protonic form. This means the progressive decrease of the number of Al in the second layer and ultimately the presence of isolated Al (site 0) with no close neighbors.

Global Basicity Cluster

This cluster involves both strong, medium, and weak basicity. It is formed from the strong basicity cluster to which is added a third layer of T sites around Al_0, i.e., at a topological distance

of 3 from this central origin 0. It is represented in Figures 5 and 6. The interconnectivity of sites is made clear in Figure 5, which indicates the atoms singly or doubly bonded from one layer to the next one. The apertures 4MR and 6MR are represented in Figure 6. The two schemes are complementary and useful for visualizing the cluster conformation. The 16 T sites of the third layer are bonded to the second shell either singly (atoms 14−16, 18, 19, 21, 23, 25) or doubly (atoms 17, 20, 22, 24, 26−29). They count respectively for $8 \times 1/4 = 2$ and $8 \times 1/2 = 4$ for the charges they bring in the framework. The other sites counting for one, the total number $x + y$ is $1 + 4 + 9 + 6 = 20$, and that of oxygens is 40. This gives the general formula $(Al_xSi_y)O_{40}Me_x$ with $x + y = 20$ and $x \leq 10$. The two six-rings of the hexagonal prism are formed for the one by sites 17, 6, 1, 13, 28 plus one site with no number (fourth layer) and for the other by sites 27, 7, 2, 0, 4, and 12. One hexagonal face of the sodalite cage is complete in the cluster (atoms 0, 3, 10, 24, 11, and 4), and the other ones belong to it by up to five sites. It may be noted with regard to the oxygen location that the square faces of the hexagonal prism contain two O1, plus one O2 and one O3 while the square faces of a sodalite cage have two O4 and two O3. Because of the basicity

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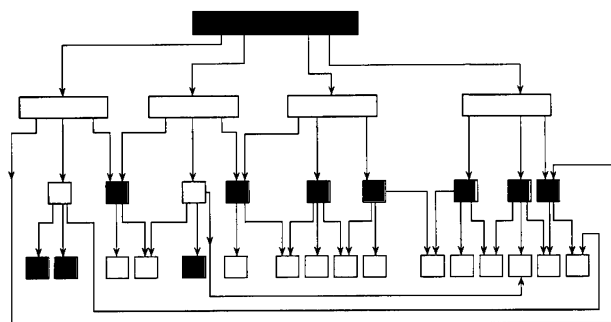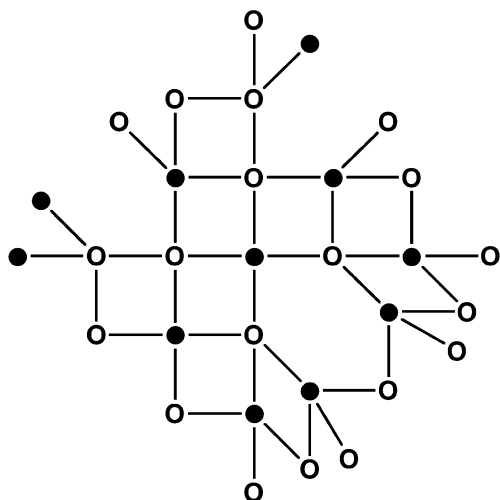
Figure 7. X_g-3 global basicity cluster drawn in two ways. Part A shows distinctly the different layers of T sites and the bonding (single or double). Part B represents the apertures (square and hexagonal). Full symbols are Al; open symbols are Si.

Figure 8. Some possible global basicity clusters for X zeolite: (●) Al; (○) Si.

difference between the oxygens, they may not be equivalent with regard to basicity.

For the X zeolite with $m_{Al} = 0.5$ derived from the cluster X_s-1 (Figure 3), there cannot be any Al in the third layer, i.e., no medium or weak sites. All the sites are strong. The formula is $(Al_{10}Si_{10})O_{40}Na_{10}$ for the sodium form. The average basicity $-\delta_0$ given in Table 1 is of course lower than for the strong basicity cluster because the charges are shared in a larger number of oxygens. In the usual X, the distribution of Al in the global basicity clusters X_g-2 to X_g-6 depends at first on the scheme considered for the strong basicity cluster. Some examples are given in Figures 7 and 8, and the cluster characteristics are reported in Table 1.

Figure 7 applies the two schemes of Figures 5 and 6 to the cluster X_g-3 and Figure 8 corresponds to Figure 6 for clusters X_g-2 and X_g-4 to X_g-6. The schemes tend to follow the models issued from ^{29}Si NMR and previously considered. To obtain an m_{Al} value close to 0.45, characteristic of the usual X, the number of medium and weak basic sites arising from the presence of Al in the third layer around Al_0 becomes of course higher when the number of strong sites is decreased in the core cluster. The values of x_g in the formulas vary from 9.5 to 8.75, and the average basicity $(-\delta_0)$ varies between 0.351 and 0.341. This is very close to the mean basicity, $-\delta_0 = 0.345$, calculated for the usual X zeolite $(Al_{86}Si_{106})O_{384}Na_{86}$. As expected, it is lower than the $-\delta_0$ strong basicity lying between 0.417 and 0.383 despite the fact that more Al are present in T sites. The number of basic sites estimated from the total number of T sites
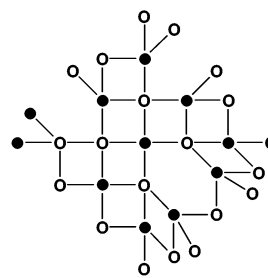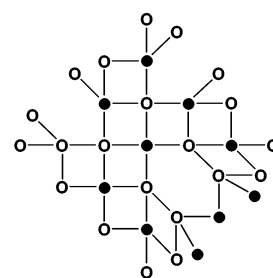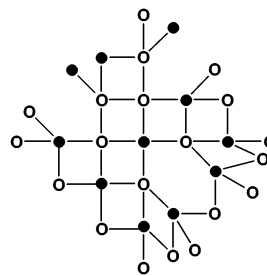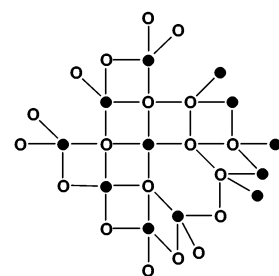
occupied by Al varies between 11 and 12 $(T_{Al}(s) + T_{Al}(mw))$. It is possible to calculate the percentage of strong sites in this number of basic sites. It is given in Table 1 by the ratio s/g of the number of strong sites $T_{Al}(s)$ to the total one. The values are in the range 82−58%. The actual values depends on the possible arrangement of the various global clusters in a crystal and of the cation present. Nevertheless, there should not be much less than around 50% of strong basic sites. Some other general remarks may be made from Table 1. For instance, starting from different strong basicity clusters, one may have the same number of T sites occupied by Al and the same global basicity (X_g-4 versus X_g-5) or a different one (Xg-3 versus X_g-4 and X_g-5). If the strong basicity clusters have a same basicity (X_s-3 and X_s-4), the corresponding global basicity may differ. As a consequence of the Al location, the percentages s/g do not follow strictly the charge of the strong basicity cluster as seen in X_g-3, X_g-4, and X_g-5. Another remark concerns the comparison of X_g-3 and X_g-6, which have the same global basicity strength, x_g and $-\delta_0$, arising from a different number of Al in T sites i.e., of basic sites. All these examples show again the importance of the Al location both in the second and in the third layer around Al_0 with regard to the distribution of basic sites and to their strength.

The suggestions for the strong basicity clusters of Y (Figure 4) may give a variety of clusters for the global basicity. Some of them, Y_g-1 to Y_g-5, are suggested in Figure 9 from the ^{29}Si NMR models already mentionned.[16−19] The molar Al ratio in the usual Y is around 0.29, which corresponds to a value of 5.75 for x_g in the formula $(Al_{5.75}Si_{4.25})O_{40}Na_{5.75}$. The strong basicity clusters bring a value of 5 for x_g (Y_g-1, Y_g-2) or 4 (Y_g-3 to Y_g-5). This leaves for the medium and weak sites a charge of 0.75 for the two first clusters and 1.75 for the others. The examples of Figure 9 fit these requirements. They generate the possibilities of having (i) one or more Al in the hexagonal face of the sodalite cages, the Al in the second case being in the meta or para position, (ii) the square faces of the sodalite with a pair of Al, and (iii) square faces of the hexagonal prism with zero, one, or two Al. Other combinations could be found. The
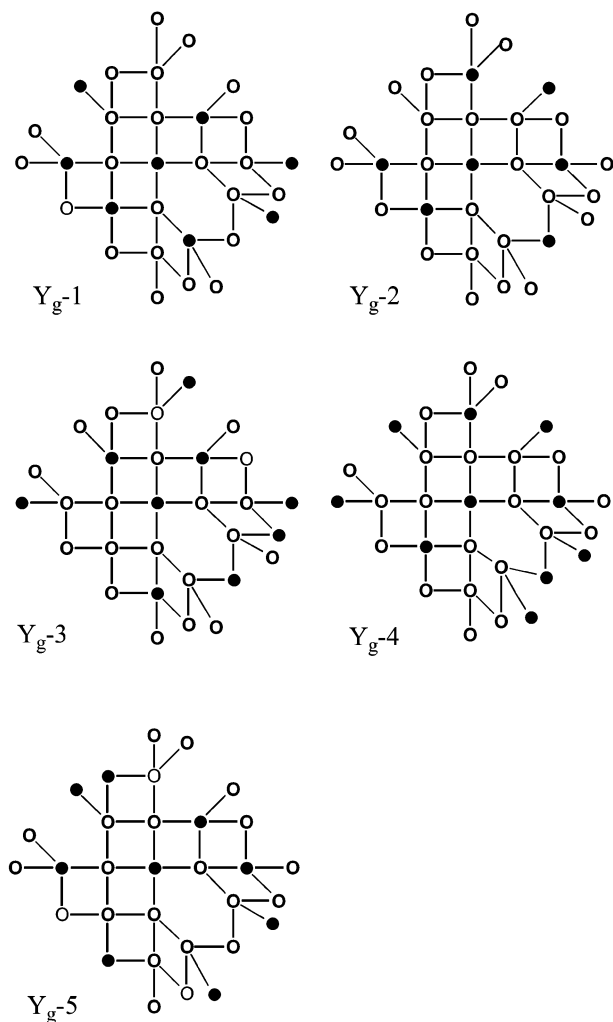
Figure 9. Some possible global basicity clusters for Y zeolite: (●) Al; (○) Si.

basic strength, expressed by x_g in Table 1, of the five clusters presented is the same despite the different Al distributions and strong basicities. The average basicity for the sodium forms $-\delta_0$ (0.301) of the various clusters is also that of the usual NaY. The percentages of strong to global basicity s/g vary between 71 and 40. The number of basic sites evaluated from the sum of T_{Al} sites lies between 7 and 10 and is lower than in X. It follows that altogether the amount of basic sites and the number and percentage of strong sites are lower in Y than in X.

The Y dealumination is known to give in the H form stronger acid sites, which means weaker bases in the cationic forms. This implies the progressive removal of Al, generating a decreasing range of basic strength. At first, the Al of the second layer around Al_0 should be eliminated and then those doubly bonded to Si of the third layer. The last ones should be the Al of the third layer singly bonded to these Si. They correspond to atoms 16, 21, 23 in Y_g-1, 19 in Y_g-2, 14, 18, 21 in Y_g-3, 14, 16, 19, 23, 25 in Y_g-4, and 16, 23, 25 in Y_g-5. It is well-known that the conditions of dealumination may give rise to different acidic and catalytic properties. There is usually a part of the structure destroyed with a reorganization in the framework. One may expect that this last change induces a new distribution of Al in line with the formation of the weakest basic sites listed above.

Discussion

The study of the faujasite basicity with the help of basicity clusters gives information not usually available. It is well

accepted that the basicity strength depends on the value of a, 1 or 2, in the species $Al_0O(SiO)_aAlO$, i.e., on the topological distance, 2 or 3, expressing the number of TO bonds between the central Al_0 and any other Al of the cluster. The closest AlO_4 groups give the strongest basicity of the oxygens, and they form the strong basicity cluster containing 14 T sites occupied by Al or Si. The medium and weak oxygens arise from the presence of Al in the third layer of TO_4 tetrahedra, i.e., in species $Al_0(SiO)_2AlO$. They form the global basicity cluster, which of course contains also the strong oxygens. The total number of T sites in this cluster is 30. The detailed study of the two clusters in faujasite, for strong and global basicity, allows one to propose some possible schemes of clusters. For each zeolite, X or Y, different Al distributions follow the trends seen in the Si,Al ordering models deduced from ^{29}Si NMR studies.[16−19] It was already said that several models could represent the NMR results. Similarly, several schemes of the basicity clusters presented might exist for the same material, with a combination of them in a crystal. The clusters presented follow the Lowenstein rule and try to minimize the number of closest Al, i.e., the AlOSiOAlO species.[18−20,24] It is noted that in the present study two kinds of AlOSiOAlO sequences have to be distinguished with regard to this minimization. The ones involving the central Al (number 0 in the clusters) are described as Al_0-OSiOAlO. They represent the strong basicity around Al_0, and their number is fixed by the m_{Al} molar fraction. The sequences not involving Al_0 but only aluminums of the second or third layers and denoted AlOSiOAlO (for example, atoms 14, 5 and 15 in X_g-3 Figure 7) are not counted for the basicity because it is calculated here, since the corresponding basic sites would be considered several times. The number of such last clusters was minimized. For instance, a global basicity cluster in Y, which would have few Al in the second layer and many in the third one, would not minimize the AlOSiOAl even if the m_{Al} value is right. In fact, the Si,Al ordering in the clusters has to be rather homogeneous because any Al may be considered as an Al_0.

The different clusters presented for the same zeolite type X or Y show how much the Al location may generate various basicities (amount and strength of sites). The basicity clusters allow a calculation to be made of their basic strength and then help to understand the effect of the Al located at such a site. An Al atom of a layer n doubly bonded to Si atoms of the layer $n − 1$ generates a stronger basic site when it is singly bonded. This confirms the importance of the topology of a framework as a main parameter to induce basicity. In addition to what is well-known about the higher basic strength of X compared to Y, the clusters presented indicate, on average, a larger fraction of basic sites being stronger in X than in Y.

Compared to previous studies on Si,Al ordering,[16−21] this approach gives more detailed information on the links with chemistry. Its goal is to show how the combination of the topology and of the basicity of a zeolite may help to understand the Al distribution in terms of chemical properties. For instance, the results indicate that it is not the location per se of Al in a square or in an hexagonal aperture that determines the basicity of the oxygens. It is the number of charges introduced in the cluster by this aluminum, i.e., the way the T sites are interconnected around it in the framework. An Al cannot be considered alone without looking at all its T sites second and third neighbors. The approach might also be applied to questions related to zeolite synthesis. What are the reasons that direct the location of Al in some peculiar sites. Does it come from the Al and Si sources, from the template, from the experimental conditions? Would it be possible to master the synthesis

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conditions to reach the best requested material, whatever it is, strongly or weakly basic, with Al in predetermined locations? Another application would be to get more information on the interaction between the basic zeolite and an adsorbed molecule or more generally the interaction between the zeolite framework with Al in specific locations and the extraframework species added to increase the basic properties.

Properties other than basicity would be relevant to this approach for studying, for instance, the exchange capacity for bivalent cations in siliceous zeolites (refs 25 and 26 and references therein) with regard to, for example, the redox behavior.[26] It is also suggested that properties related to the presence of atoms other than Al and Si (Fe, Ti, Ga, Ge, P in Sapo's, ...) may be considered with the use of clusters built around a central atom.[14] Such clusters can be more generally termed *topological clusters*. In SAPO-37, which has the faujasite structure, a detailed study of the topological environment of Al, Si, and P was correlated to different acidic and catalytic properties.[27] The approach would also be relevant to the studies of other micro- or mesoporous materials such as MCM materials, for instance, where a local description of a site would be of interest.

The correlation between the basicity clusters and the acidity can be studied more deeply. The framework oxygens are fixed except for some slight relaxation. The distribution on the oxygens of the charges introduced by the Al atoms depends on the Al content, on the metal cations present (identity, content, ...),[8,9] and on some other factors such as the presence of an adsorbed phase such as benzene,[2,28,29] the pressure, or the temperature.[2] In acidic materials the protons of the hydroxyl group are mobile and may jump easily from one framework oxygen to the other one in AlO_4 tetrahedra. It follows that the distribution of negative charges on these oxygens may be very different from that observed in basic zeolites. For example, it is known that the most acidic protons belong to O1H and O3H groups.[30] This would not be in line with the classical rule in chemistry, which links a strong acid to a weak base because O1 is one of the most basic oxygens (with O4) in the cationic faujasite.[8] In fact, this means that in faujasites, in the actual protonic form O1 is a weak base and it is a strong base after exchange with a metal cation. Nevertheless, some general trends might be driven from information brought by basicity clusters at very low Al content where a spontaneous proton transfer occurs with water and the protons are located close to the Al.[31] The protonic siliceous faujasites are known to a have stronger acidity than Y and quite more than X. This was related to isolated Al, i.e., to $Al_0O(SiO)_aAlO$ sequences with $a > 2$ [31] or at least to only few moieties with $a = 2$. At this topological distance of 3, a cluster centered on Al_0 and with only one Al atom singly bonded gives a mean molar fraction $m_{Al} = 1.25/20 = 0.06$ and a doubly bonded one gives $1.5/20 = 0.075$. Many experimental measurements of acidity and cracking catalytic activity of dealuminated faujasites were conducted.[31] They showed that an m_{Al} value of around 0.14 for faujasite corresponded to the acid strength of an 88% H_2SO_4 solution. The cracking activity did not rise at lower m_{Al}, indicating no major effect of stronger acid sites that could eventually be formed in the zeolite. To consider that the $m_{Al} = 0.14$ value is the lower limit of the presence of $Al_0O(SiO)_2AlO$, as was proposed before, is probably too simple. More likely, many of the Al located in the third layer around Al_0 would probably still be present in protonic zeolites for this m_{Al} value. When the Al content is decreased in Y (0.29) to this 0.14 value, the acid strength linked to the Al is increased to an acid strength high enough to catalyze

the cracking reactions considered (around 88% H_2SO_4). When this acid strength is reached, removing Al below the m_{Al} value decreases the total number of active sites independently of any further increase in the strength, which is not needed and not detected in the catalysis of these reactions. The existence of some $Al_0(SiO)_aAlO$ species in this m_{Al} domain 0.14−0.06 is consistent with the case of other highly siliceous zeolites.[25,26] In ZSM-5, for instance, for a mean m_{Al} of 0.077 (Si/Al = 12) a theoretical calculation showed that 64% of the Al would form AlOSiOAlO species[25] and an experimental study for Si/Al = 12.5 says that 40−80% of the Al would be present as AlO-$(SiO)_2AlO$ sequences.[26] These values are in line with $m_{Al} = 0.06$ or 0.075 reported above for the expected disappearance of the $Al_0(SiO)_2AlO$ species in faujasite.

Conclusion

As an application of the framework-induced basicity, the approach of the faujasite basicity estimated from the basicity clusters suggests the proposal of several schemes for the Al location in X, Y, and dealuminated zeolites. They are in line with the Al distribution issued from ^{29}Si NMR studies and with the existence of a range of basicity known from experimental results. The clusters allow an estimation to be made of the amount of oxygens involved and of their basic strength. The X zeolites contain not only the largest amount of strong basicity but also the highest percentage of strong sites. The key to generate strongly basic oxygens is to locate the Al in a layer n at a site where it is doubly bonded to Si atoms of the layer $n - 1$. The understanding of the importance of the Al location at a molecular level opens new opportunities to generate faujasites, or other zeolites, with a predetermined basicity. More generally the example of basicity may be extended to other chemical properties of microporous or mesoporous materials that depend on the presence of several types of atoms in a crystal. The topological clusters would be useful to consider in such studies.

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