ISOMORPHIC SUBSTITUTION IN ZEOLITES : ITS POTENTIAL CATALYTIC IMPLICATIONS

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I. INTRODUCTION

Isomorphic substitution in high-alumina zeolites : the first generation materials

The replacement of isomorphous elements in a crystalline lattice, i.e. of elements with similar cationic radii and coordination requirements, has also been reported for the class of synthetic zeolites. When the term isomorphic substitution is used for these compounds, it refers to replacements of T-atoms, i.e. atoms tetrahedrally coordinated to oxygen atoms. Commonly encountered T-atoms are silicon and aluminum. In the early literature, reviewed by Breck [1], as potential candidates are described for substitution in tetrahedral sites : Ga^{3+}, P^{5+}, Ge^{4+} and Fe^{3+}. The existence of Zr-, Ti- and Cr-silicate "zeolites" has been claimed as well. By the same author it was stated that " at this stage boron incorporation in a zeolite had not been achieved". All this work refers to substitution in so-called first-generation zeolites with low silicon content. The main arguments that proof the existence of the replacement of T-atoms by isomorphic ions are :

i) the change of the unit cell dimensions with the degree of substitution. In faujasite-type zeolites, the contraction of the cubic unit cell seems to be correlated linearly to the degree of substitution of Al for Si [2]. The same kind of relation was shown to hold when in an A-type aluminosilicate structure, phosphorus was incorporated : at increasing degree of P incorporation, the unit cell was also found to contract [3].

ii) the gradual shifts of the lattice vibrations with the degree of substitution. This correlation has been established by Flanigen [4] for faujasites with different Si/Al ratios. Depending on the particular nature of the normal vibration, the susceptibility of its frequency to shifts is different.

The existence of a general equation, describing the unit cell parameters as a function of the Al content of the framework has been discussed. Indeed, Dempsey et al. [22] have reported discontinuities in this relation at 80,64 and 52 Al atoms per unit cell. Smith [23] argued about the statistical reliability and accuracy of

the chemical analysis of the data of Dempsey et al. [22]. Kühl, [24], however, reported the synthesis of gallosilicate faujasites with no aluminum and with a number of gallium ions per unit cell varying between 49 and 80, approximately. With the larger gallium ion (compared to aluminum) even more distinct breaks are observed in the relationship. The lattice parameters of the high-silica faujasites (less than 54 Ga/U.C.) deviate from this relation, as a result possibly of the presence of amorphous silica. In a recent publication Beyer et al. [25] showed that when the Breck-Flanigen equation is extrapolated to low Al contents, the regression line is parallel to their equation used to fit the a_0 - Al content data for $SiCl_4$-treated NaY :

$$a_0 = 8.68 \ 10^{-4} \ N_{Al} + 2.425$$

in which N_{Al} is the number of Al atoms per unit cell and a_0, the cubic lattice constant in nm.

These substitutions have all been realized during synthesis, and in case of the replacement of Al for Si, the degree of substitution is rather limited. For other metallosilicates, as zirconium and titanosilicates, the degree of substitution of Al was complete but in agreement with Breck [1] we believe that their characterization was insufficient to proof univocally that the claimed material was also obtained in reality. The isomorphic replacement of silicon by germanium is another reported and proved example in which the substitution was complete and the characterization sufficient [5-7]. Materials with different structure but low silicon content were obtained (faujasite and philipsite). It should be stressed that only the germanium equivalent of zeolite X has been synthesized but never a material with enhanced germanium content, equivalent to Y-zeolite could be made.

A third example of isomorphic replacement consists in the synthesis of aluminoberyllosilicates. Such materials have been reported with the faujasite [26] as well as the mordenite [27] structure. In Fig. 1 the contraction of the cubic unit cell of faujasite is plotted for such samples, at two different Al/Be ratios. This figure shows that the regression lines for the two families of materials change in an almost parallel way with the Al content. The effect of the Be content of the faujasite is much less pronounced. This is not unusual since Be^{2+} and Si^{4+} have similar ionic radii (see later). Possible substitution mechanisms are [26] :

$$2(AlO_2)^- = (BeSiO_4)^{2-}$$
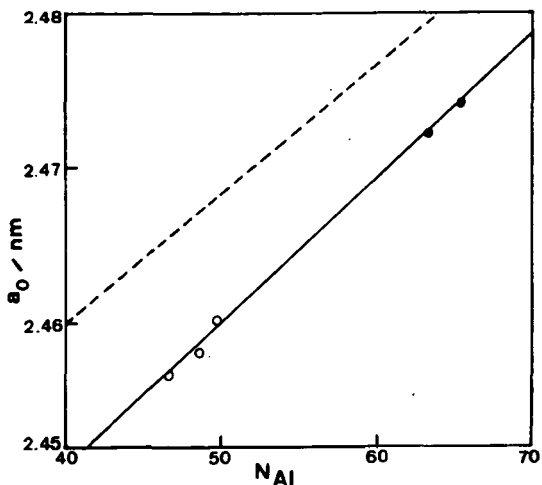
$$(AlO_2)^- = |BeO(OH)|^-$$
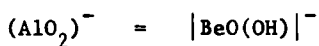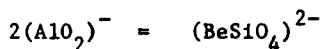
FIG. 1. Unit cell contraction of aluminoberyllosilicates with faujasite structure with different Al and Be concentrations. The open points refer to samples with $BeO/Al_2O_3 \cong 0.40$, the full points to BeO/Al_2O_3 ratios of 0.20, approximately. The experimental data are from ref. 26, exs. 1-5, the dashed line corresponds to the Breck and Flanigen correlation [2] for aluminosilicates with faujasite structure.

Arguments which point to the incorporation of Be in the faujasite lattice are :

    i. the different a_0 values obtained for alumino- and aluminoberyllosilicates with the same structure (Fig. 1), the a_0 value being lowest for the Be-containing zeolite.

    ii. the possibility to synthesize easily faujasites with high Si/Al ratio in presence of Be. Values above the critical BeO_2/Al_2O_3 ratio of 6 can be obtained in the Be-Al-Si-system [26].

    Recently, Beyer and Belenykaya [8] were able to show that by the following solid state replacement reaction, faujasite structures with Si/Al ratios varying between 2.5 and infinity could be obtained easily :

$$Na_x (AlO_2)_x (SiO_2)_y + SiCl_4 \rightarrow Na_{x-1} (SiO_2)_{y+1} + NaAlCl_4$$
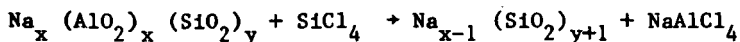
The contraction was again described by a regression line parallel to the ones given in Fig. 1 [25]. Preparation of aluminum-deficient faujasites and mordenites can be achieved by a wide variety of methods, giving materials with variable properties, as far as crystallinity, and concentration of defect sites is considered. This particular matter has been the subject of a recent review [9].

Only in case of SiCl$_4$ [8] and (NH$_4$)$_2$ SiF$_6$ aqueous solutions [10], the substituting element is of extra-lattice origin. All the classical dealumination methods, such as hydrothermal treatment of NH$_4$Y [11], reaction with chelating agents [12], acids [13] or treatment with F$_2$ gas [14] or combinations of these methods, in a first step seem to form defect sites, consisting of hydroxyl nests. In suitable reaction conditions these holes, have to be filled up with silicon atoms originating from amorphous parts of the zeolite lattice. In this way defectuous structures have to be formed, mainly characterized by the occurrence of a secondary porosity and the generation of a bidisperse pore size distribution [15].

Isomorphic substitutions in high silica-medium pore zeolites : the second generation materials.

In this new generation of zeolites with medium pore size and high silica content, extensive substitution of aluminum for silicon seems also possible. The existence of a series of ZSM-5 zeolites with continuously varying Si/Al ratios in the framework structure has been proven and gives the so-called ZSM-5 substitutional series [16] . Even the aluminum-free structure types, can be synthesized and give rise to the existence of crystalline silica polymorphs with a zeolitic structure type. Silicalite 1 [17], silicalite 2 [18] and TEA-silicate [19] belong to this family of new materials. They all can be obtained by direct synthesis. Further variation of their composition can occur by the classical dealumination methods as steaming. Realumination of such structures with aluminum halides seems to be possible via an aluminum insertion during a high-temperature gas-solid reaction [20,21] , at least to a limited extent [21] . The opposite reaction of this alumination was shown to be possible with fluorosilicate solutions as driving force [10].

In the recent patent literature a whole variety of metallosilicates with medium pore size and high silica content has been claimed. A non-exhaustive enumeration of such materials is given in Table 1.

Table 1 shows that apparently numerous possible substitutions can occur in these high silica structures with medium pore sizes. Generally speaking these new materials are claimed based upon their novel chemical composition or XRD spectrum or both. This novelty doesnot necessarily mean that the new materials contain the new element, or at least part of it, substituted in the zeolite framework. As far as we are aware, only in the case of boron substitution sound proof is available for its presence in the zeolite lattice :

1. the unit cell volume of these zeolitic borosilicates was found to decrease monotonously with the degree of B-substitution [44]. The phenomenon can be described by the following theoretical regression line [44] :

$$V_B = V_{Si} - _{Si} \left[1-(d_B/d_{Si})^3 \ x \right]$$

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TABLE 1

Survey of different metallosilicates claimed in patent literature

NATURE OF SILICATE	Si/Me	Si/Al	REMARKS	REF.
AMS-1B borosilicate	52.3	1410	Specific XRD	28,ex.1
ZBH borosilicate zeolite	48.8	–	Pentasil-type	29,ex.1
Boroaluminosilicate	4.5	1667	Offretite-type	30,ex.1
Boralite	120.0	–	Various structures	31,ex.1
Gallosilicate	68.3	–	THETA-1	32,ex.1
Chromesilicate zeolite	86.8	275.1	MFI	33,ex.1
TRS-27 : beryliumsilicate	12.0	–	–	34,ex.1
TRS-66 : zincsilicate	15	–	–	34,ex.3
TRS-64 : titaniumsilicate	3	–	–	34,ex.6
TRS-48 : vanadiumsilicate	17	–	–	34,ex.7
Titanoaluminosilicate	21.3	87.0	MFI	35,ex.1
Zirconoaluminosilicate	28.6	76.9	MFI	36,ex.1
AMS-1 Cr chromosilicate	32.6	1515.2	AMS	37,ex.4
Zincosilicate	0.8	–	Zeolite A	38,ex.2
Zincaluminumsilicate	13.4	94.5	–	39,ex.1
Arsenesilicate	207.3	375.2	Zeolite structure	40,ex.1
Organosilicate containing tin	7.6	1787.0	Zeolite	41,ex.1
Iron-silicate	200	0.0	Zeolitic	42,ex.7
Iron-alumino-silicates	23.0	163.1	MFI	43,ex.1

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in which V_{Si} and V_B stand for the unit cell volume of the silicate and B substituted form, respectively and x corresponds to the B fraction of the T-atoms.

ii. a discrete boron NMR signal is found in such materials and has been assigned to tetrahedrally coordinated boron in the structure [45,46].

Third generation molecular sieve zeolites.

The recent discovery of a new family of zeolites shows that isomorphic substitution in the $(Si_x Al_y P_z)O_2$ system is possible over a very wide range [47,48] . They are denoted as SAPO-n in which n refers to a particular structure-type. Up to 13 tridimensional microporous frameworks have been reported till now [48] . In contrast to these SAPO's, the AlPO family of aluminophosphate molecular sieves [49,50] consist of tridimensional $(Al-P)O_2$ frameworks. As a result of the valency of the cations (Al^{3+}, P^{5+}), these materials do not contain any excess of negative charge in tetrahedral coordination with oxygen. These materials have therefore no exchange capacity and have to be classified as molecular sieves instead of as zeolites. SAPO zeolite structures are considered to be derived from the corresponding aluminophosphate framework by substitution of silicon for phosphorus or by simultaneous substitution of 2 silicons for one aluminum and one phosphorus [48].

After this short review of the state of the art in matters of isomorphic substitution in zeolites, an attempt will be made to predict the effect of this substitution on catalyst activity and selectivity, using general and basic chemical principles more in particular the MFI-structure type will be considered and the general rules will eventually be illustrated with literature or new experimental data.

II. ATTEMPT TO PREDICT THE CATALYTIC IMPLICATIONS OF ISOMORPHIC SUBSTITUTIONS IN ZEOLITES USING GENERAL CHEMICAL PRINCIPLES

### Possible types of isomorphic substitutions

When in a crystalline microporous silica polymorph with zeolite framework, ions of different valency state are substituted, the following possibilities exist :

i. for a substitution with a tetravalent ion the framework remains electrically neutral;

ii. for every trivalent ion incorporated in such a structure, a negative charge will have to be compensated for;

iii. with the incorporation of a bivalent ion, the creation of two negative charges is associated if tetrahedral coordination is strictly obeyed; otherwise oxygen defect sites will make the lattice electroneutral;

iiii. when a pentavalent ion is incorporated an excess positive charge exists. In order to behave as a cation exchanger, T-atoms with formal charge of 2 or lower, have to be present at the same time. Potential sites formed in this way, with protons as charge compensating ions, can be schematically represented as follows :
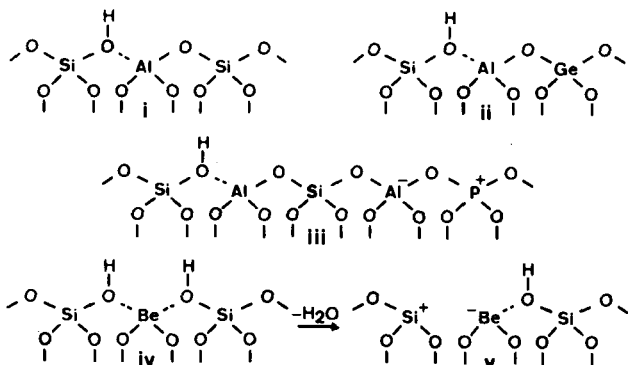
———— : chemical bond; ---- : formal coordination link

The scheme shows that incorporation of Me^{2+} forms two silanol groups in close proximity (iv), which are expected to be very susceptible to dehydroxylation (v) and result possibly in elemination of $Me-O_x$ and structural rearrangements. Incorporation of pentavalent ions generates a SAPO-type structure with a relatively high Al and low proton content.

Substitution with Me^{3+} T-atoms gives an increased number of Brønsted sites (i), the strength of which can be varied by substitution with Me^{4+} of different nature (ii). These qualitative considerations already suggest that SAPO-type materials for an identical number of Brønsted sites will contain a lower Si/Al ratio than the corresponding aluminosilicate and since Brønsted acid strength decreases with increasing aluminum content [51] , they will show lower Brønsted activity. This is also experimentally observed in the cracking of n-butane [48] . The effect of the nature of the T^{4+}-atom on the Brønsted acid site strength was confirmed for the silicon- and germanium analogues of zeolite X : in the dehydration of tertiary-butanol, the former material - all other factors remaining the same - was by far the more active [52] . In some particular reactions, because of the low uniform Brønsted acidity, secondary reactions and coke formation are suppressed on the germanium-substituted faujasite [52] .

Requirements for tetrahedral coordination

Stable tetrahedral coordination of the substituting elements will be determined by the size of the T-atoms. A possible measure for this can be the ionic radius. Ionic radii from several literature sources for pertinent ions are given in Table 2.

TABLE 2

Ionic radii of elements susceptible for substitution in a zeolite framework and their minimum radius ratio "R", in a Me-O matrix

ION	PAULING[a]	GOLDSCHMIDT[b]	SCHANNON[c]	R[e]
$Si^{4+ d}$	0.41	0.38	0.40	0.37
$Ge^{4+ d}$	0.53	0.54	0.53	0.43
Cr^{4+}	-	-	0.55	-
Ti^{4+}	0.68	0.60	0.56	0.55
Sn^{4+}	0.71	0.71	0.69	0.55
Zr^{4+}	0.80	0.77	0.73	0.62
Hf^{4+}	-	-	0.72	-
$B^{3+ d}$	0.20	0.2	0.25	0.20
$Al^{3+ d}$	0.50	0.45	0.53	0.41
Fe^{3+}	-	0.53	0.63	0.45
Cr^{3+}	-	0.55	-	-
$Ga^{3+ d}$	0.62	0.60	0.61	0.46
$Be^{2+ d}$	0.31	0.30	0.41	0.25
Mg^{2+}	0.65	0.65	0.71	0.47
Zn^{2+}	0.74	0.69	0.74	0.50
As^{5+}	-	-	0.475	0.40
$P^{5+ d}$	-	-	0.31	0.34
V^{5+}	-	-	0.495	0.50
Cr^{5+}	-	-	0.485	-

a, ref. 53; b, ref. 54; c, ref. 55; d, for these ions there exists firm experimental evidence that they can be incorporated in a zeolite matrix (see introduction); a, radii in octahedral and c, in tetrahedral coordination; e, derived from ref. 53.

Based on this table and the evidence mentioned in the introduction, elements with ionic radii between 0.020 and 0.061 nm are potential candidates for incorporation into a framework, and most of the claimed elements possibly fit as T-atom in a zeolite matrix.

A more accurate estimate of the potential of given cation to be tetrahedrally coordinated in an oxygen matrix of anions is available. Pauling defined for this the concept of minimum radius ratio, R, which determines the stability of various coordination polyhedra or the preferred ligancy of a cation [56]. According to Pauling stable tetrahedral coordination can be formed for $0.225 < R < 0.414$. Using this criterion it is obvious that B^{3+} will prefer trigonal coordination in a zeolite matrix. It follows that the B-analogue of species i will be relatively unstable. B-substitution may therefore give rise easily to the formation of defect sites in which trigonal coordination is favoured.

Using the minimum radius rate concept, it can be understood that upon substitution of P for Si the unit cell volume of zeolite A decreases [3], as well as when Si is substituted for Al in faujasite frameworks [2]. It also explains that boralites show a decreased unit cell volume when boron is incorporated in a silicious zeolite [44]. Neglecting the contribution of differences in T-O-T bond angles upon substitution, the unit cell contraction of a given structure will be determined by R. In Fig. 2 are shown the change of the unit cell volume when elements with suitable R are substituted in the framework of a silica polymorph.
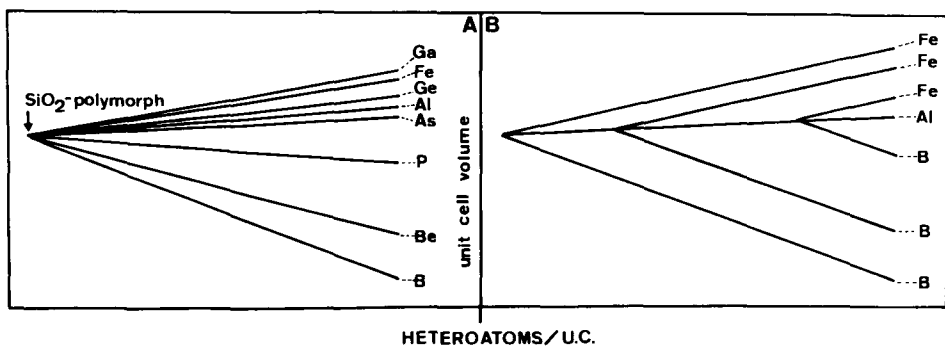

Fig. 2 Schematic representation of the changes in the unit cell volume of a silica polymorph upon isomorphic substitution of Si for one (A) or two different (B) elements.

The slope of the lines is proportional to $(R_{Si-O} - R_{Me-O})$.

Fig. 2 further shows that a wide range of changes in the volume of a unit cell may be achieved when judiciously selected elements are incorporated. It explains why AMS-1B zeolites show high p-xylene yields [57] in alkylation or isomerization reactions. The absolute value of these contractions is expected to be dependent on the structure type but it is clear that even subtle changes in the effective size of medium pore zeolites may induce pronounced changes in reaction selectivity. Typical examples of such effects are reported when the MFI-structure type is changed for the MEL-structure type [58].

In conclusion, it may be stated that many elements which on pure chemical grounds are claimed to be occluded in medium pore silica zeolites, are susceptible for being substituted in such frameworks as can be derived from the argumentation of this paragraph. Substitution of selected elements can also induce predictable changes in the unit cell dimensions and affect reaction selectivity.

Isomorphic substitution and changes in Brønsted acid strength

Changes in Brønsted acidity upon isomorphic substitution in aluminosilicates can be rationalised in terms of the average Sanderson electronegativity [51]. In fact, in this picture the acid strength of an OH group vibrating in a zeolite pore is then determined by the chemical composition of the environment. This relation holds only for an homologous series of materials, as e.g. a silica polymorph with the MFI structure in which different elements are substituted. In Fig. 3 is shown, therefore, the change of the average Sanderson electronegativity, S, when different elements are incorporated, which according to the coordination requirements are susceptible to substitution.
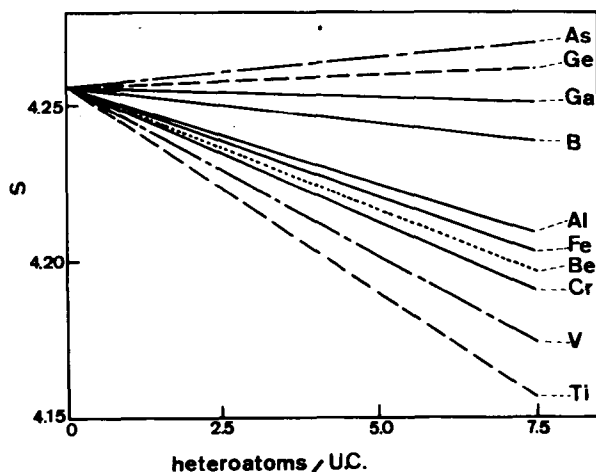

Fig. 3 Change of the Sanderson electronegativity, S, of a silicon polymorph with a MFI-structure in which foreign elements are substituted to different extents.

The figure shows that depending on the nature of the substituent and its amount incorporated, the Sanderson electronegativity and consequently the overall Brønsted acidity of such a material which contains protons, can be varied over a wide range. It follows also that given their higher S values, boron and galliumsilicates should exhibit stronger acidity than the corresponding aluminumsilicates. There is at least one example in literature which experimentally indicates an opposite trend : the boralite family of zeolites in the decomposition of methyltertiary butylether (MTBE) is found to be less acidic than ZSM-5 [44].

Since most reactants to prepare silica polymorphs contain impurity elements, as e.g. Al, changes in S were also calculated for the case of a silica polymorph with MFI structure containing 5 heteroatoms as well as for a material containing 5 aluminum next to 5 heteroatoms. The effect of these substitutions in MFI can be followed in Fig. 4.
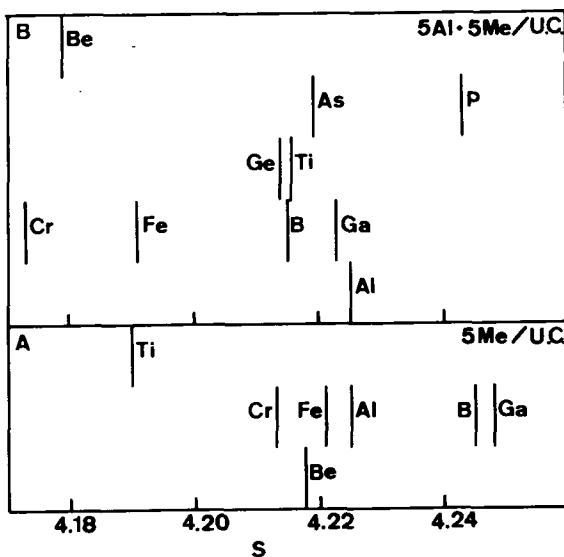

FIG. 4. Effect on the average Sanderson electronegativity, of isomorphic substitution in a silica polymorph with a MFI-unit cell : A, incorporation of 5 heteroatoms per unit cell; B, substitution of 5 Al next to other heteroatoms.

When two kinds of heteroatoms are present, the average S now decreases from the aluminosilicate to the aluminoborosilicate system. This is in line with the results obtained from the MTBE reaction [44]. From a selection of the literature on heteroatom incorporation into such systems [22-44], it is evident that each

material has residual Brønsted catalytic activity. However, no systematic comparison has been made of the effects of these substitutions.

We decided to synthesize therefore several MFI-type metallosilicates containing the following heteroatoms : Al, Al + B, Al + Fe, and Al + Be, covering in this way a relatively wide change in S, as well as in unit cell contraction. The changes in catalytic properties of these solids were followed in the n-decane isomerisation-hydrocracking reaction. The activity of a catalyst in this reaction can be rationalised in terms of its S value [51] and the selectivity is affected by minor changes in the pore sizes and void structure [59].

III. n-DECANE HYDROCONVERSION OVER MFI ZEOLITES WITH VARIOUS HETEROATOMS

The experimental procedure to follow the n-decane isomerization-hydrocracking reaction has been described in extenso [59]. ZSM-5-type zeolites were synthesized according to the diluted method described by Von Ballmoos [60]. Al, Be, Fe were added as nitrates, B as H_3BO_3. Changes in the OH^-/SiO_2 ratio provoked this way were compensated with NaOH. The samples contained each 0.20 $\pm$ 0.08 Al atoms per unit cell. The Me content measured after washing and NH_4-exchange was 1.6 $\pm$ 0.2 Me atoms, assuming that they all are substituted in the framework. The conversion of these NH_4-(Me)-ZSM-5 zeolites into bifunctional catalysts containing 1 % Pt is also described in earlier work [59,60]. The samples will be further denoted by the nature of the heteroatoms followed by their concentration in the solid as possible heteroatoms per unit cell. The crystals in each case have an hexagonal shape of 6 x 10 μm, approximately.

Influence of substitution on the activity

The overall activity of the $Al_{1.6}$, $B_{1.6} - Al_{0.2}$, $Fe_{1.6} - Al_{0.2}$ and $Be_{1.6} - Al_{0.2}$ samples is given in Fig. 5A, together with that of an $Al_{0.2}$ sample. A series of parallel curves is obtained, displaced with respect to each other on the temperature ascis. The data allow to make two general statements :

i. there has been incorporation of B, Fe or Be in the MFI-structure. Indeed, the overall activity is definitely higher than due to the presence of residual aluminum.

ii. the activity sequence :

Al > B > Fe > Be

is the one predicted by the Sanderson electronegativity of such systems (Fig. 4).

Another proof for the incorporation of these elements in the structure and for their relative stabilizing such environment can be derived from the change in catalytic activity after high temperature calcination of the samples (Fig. 5B).
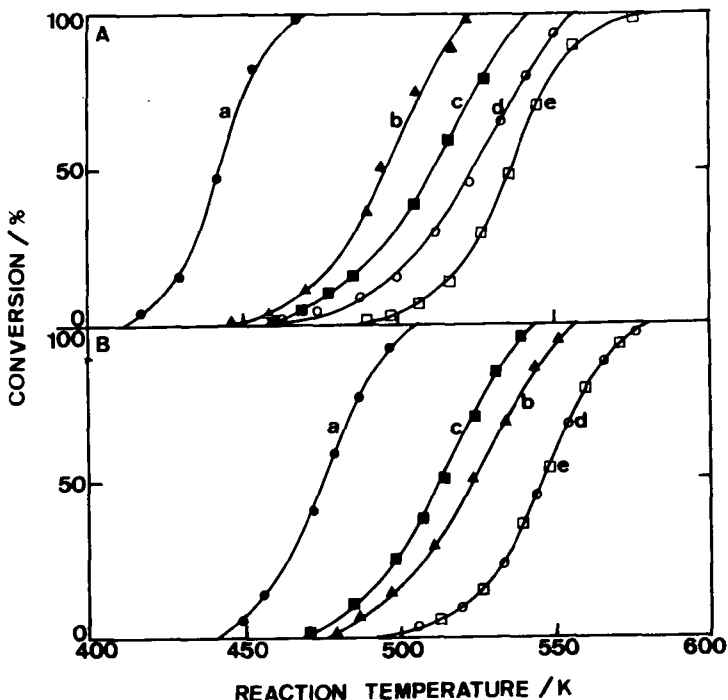

Fig. 5. Overall hydroconversion of n-decane on Me-containing zeolites of the MFI-structure type. A, samples precalcined at 823 K and B at 973 K : a, $Al_{1.6}$; b, $B_{1.6} - Al_{0.2}$; c, $Fe_{1.6} - Al_{0.2}$, d, $Be_{1.6} - Al_{0.2}$ and e, $Al_{0.2}$.

After calcination at 973 K, the activity of the Be-sample has decreased to the level of the reference Al-sample. This probably indicates that under such severe conditions all lattice Be has been removed. When the behaviour of the B, Be and Fe samples is compared, it can be derived that the stability of the respective ions in the tetrahedral coordination of the MFI-structure should decrease as follows :

Fe > B > Be

This same sequence could have been derived using the general concepts on which has been elaborated in previous section.

The overall isomerisation-hydrocracking selectivity in the bifunctional conversion of n-decane is also governed by acid strength [51]. All other factors, as competitive sorption-desorption, remaining equal, the Brønsted acid strength will determine the life-time of the carbocation intermediates. For longer

life-times, caused by stronger acidity, the probability for cracking will increase
with respect to isomerization. The selectivity towards feed isomerization is
therefore expected to increase as follows (Fig. 4) :

Al > B > Fe > Be

That this is observed in actual reaction conditions is illustrated in Fig. 6
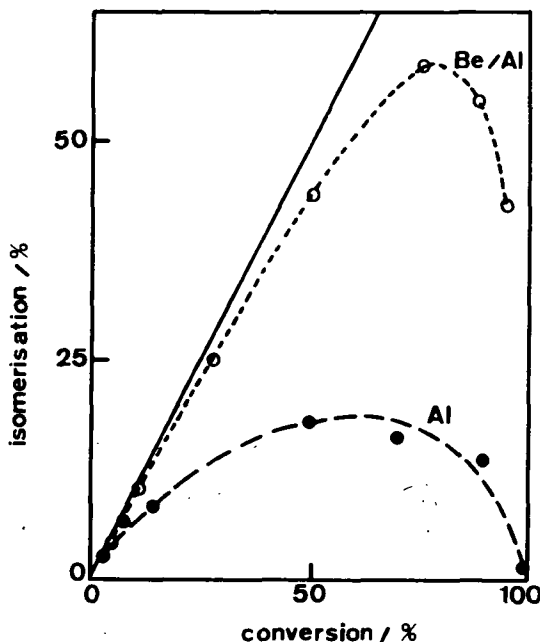for the two extremes of this series of materials.

Fig. 6. Isomerisation-hydrocracking selectivity in the conversion of n-decane
over $Al_{1.6}$ and $Be_{1.6} - Al_{0.2}$ substituted MFI-structure types.

Effect of isomorphic substitution on product selectivity

It has been shown that hydrocracked products are formed via a consecutive
β=scission reaction on multibranched isomers [61] . Central cracking is most
probable on highly branched isomers, preferentially with branchings in α,α,γ
-positions. It follows that in case of n-decane, the amount of isopentane formed
will be strongly dependent on the nature of the intermediate isomers in the inner
void structure in a particular zeolite. These isomers not necessarily desorb.
Therefore the absolute yield of isopentane formed will be very susceptible to small

changes in the zeolite pore size [59]. In the present case, this yield is expected to decrease when lattice contraction occurs. The data of Fig. 7 confirm this again with experimental data.
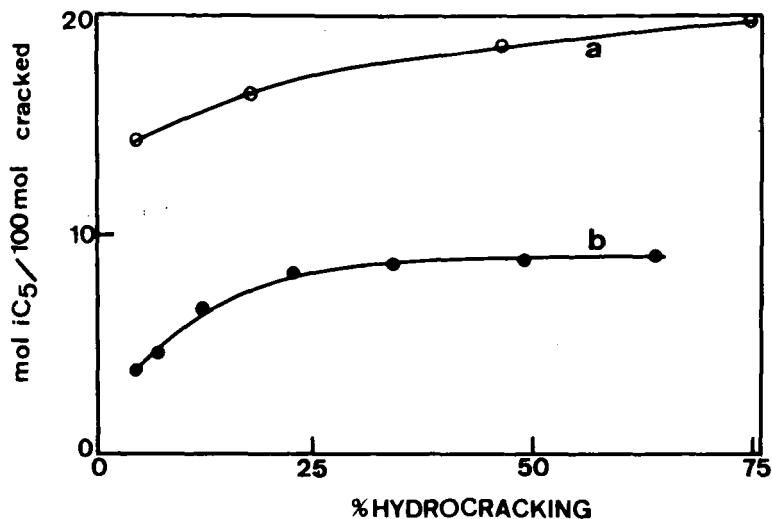

Fig. 7. Absolute yield of isopentane formed from n-decane at increasing hydrocracking conversion : a, $Al_{1.6}$ and b, $Be_{1.6} - Al_{0.2}$ samples.

The decreased isopentane yield on the $Be_{1.6} - Al_{0.2}$ sample compared to the $Al_{1.6}$ ZSM-5 zeolite, can be interpreted as a decrease in unit cell volume upon replacement of Si by Be, just as predicted by the general considerations developed earlier.

IV. CONCLUSIONS

Literature as well as new experimental data confirm the conclusions on isomorphic substitution of foreign elements in zeolite aluminosilicates. Based on general principles the nature of the ions which are potential candidates for substitution has been determined. Such replacement has consequences for the size of the unit cell of a zeolite and for the strength of Brønsted acid sites. This has implications for both catalytic activity and selectivity. A judicious selection of several elements for substitution in zeolite frameworks may give a zeolite with a tailor-made porosity and acid site strength. Much remains to be done in the area before it will be possible to advance further generalization.

V. ACKNOWLEDGMENTS

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