# Exploration of the void size and structure of zeolites and molecular sieves using chemical reactions

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Abstract – An overview of chemical reactions is made which in the literature are proposed to be of help in the exploration of the intracrystalline void volume of zeolites and molecular sieves. The potential and limitations of the following conversions are considered in detail : the simultaneous catalytic cracking of hexane and 3-methylpentane (the so-called constraint index) and of longer paraffins; the conversion of xylenes; the n-decane bifunctional conversion; the bifunctional conversion of naphtenes and the disproportionation of ethylbenzene. Also new data are added which illustrate certain aspects of this way of zeolite and molecular sieve characterization. So, it is illustrated that the new microporous crystalline polyoxides patented by Union Carbide can be quickly characterized.

## ADVANCED TECHNIQUES AVAILABLE TO DETERMINE VOID SIZE AND STRUCTURE

The discovery of new materials in the area of zeolite science and their use as highly active, selective or stable catalysts of chemical transformations occurs no longer by chance but is often only the result of a systematic effort in synthesis and modification. This requires that in a short time a large number of crystalline solids has to be characterized in terms of pore size and void structure of these materials.

X-ray diffraction (XRD) on powders will always remain a basic technique to determine the degree of crystallinity and phase purity of new materials. Scanning electron microscopy (SEM) is an irreplaceable method to determine average crystal sizes, crystal size distribution and sample morphology. The exact determination of the crystal structure of a new and/or modified zeolite and molecular sieve requires lenghty and expensive procedures as well as highly advanced expertness. Indeed, only precision XRD can be used to determine crystal symmetry, unit cell dimensions and space point groups (ref. 1-3). Only when single crystals are available (with a diameter of at least 40 µm), a combination of this direct method with model building, calculation of atom coordinates from these models with a distance least square program (DLS) (ref.4) can be used to solve the structure of the new crystalline solid (ref. 1 - 3,5). Structure solution of crystalline powders in the 1 to 10 µm range can be achieved using the diffraction of both electrons and X-rays in combination with the already mentioned trial and refinement procedures (ref. 6-9). Supplementary information on the presence of distinct crystallographic sites is available from MASNMR (Magic Angle Spinning NMR) (ref. 10).

In a few places, neutrons from a high flux beam nuclear reactor are available for powder diffraction work (ref. 12). It seems that reliable structural information can be derived from powder neutron diffraction data on samples with known structures. The same can be done using specific XRD sampling and refinement techniques (ref. 11,13). All these procedures provide only spatially averaged information, while High Resolution Electron Microscopy (HREM) used in conjunction with Selected Area Electron Diffraction (SAED) can be used to probe the local crystalline structure and detect defective or multi-phasic areas (ref. 14-16).

It is evident that none of these methods can be used as routine procedures for the characterization of the void size and structure of zeolites. Moreover, the information refers to room temperature in presence of sorbed water or in absence of any sorbed molecule. Only in exceptional cases (ref. 17), structural information in catalyst working conditions has been determined using XRD. The desire to characterize zeolitic void spaces in working conditions as catalyst is far from academic since zeolite ZSM-5, one of the more stable specimen, is known to change its symmetry from orthorombic to monoclinic after specific thermal treatments and to undergo at room temperature sorbate induced structural changes (ref.19).

## ESTIMATION OF THE PORE SIZE OF ZEOLITES AND MOLECULAR SIEVES USING SORPTION TECHNIQUES

Effective pore size of new materials has often been determined for patent purposes (ref.20, 21, 23, 24) by sorption of molecules with systematically increasing diameters. This approach is not new since the pioneering work is reported by Breck (ref. 22). Oxygen sorption at 90 K seems to give a good estimate of pore volume, as well as the water sorption capacity. The latter values, however reflect also differences in hydrophobicity when materials with different chemical compositions are compared. The sorption of hydrocarbons with increasing kinetic diameter is then able to determine the effective pore size within relatively narrow limits. Fig. 1 illustrates this for silicalite, ZSM-5, NaY, ALPO-5, TAPO-5 and TAPO-11.
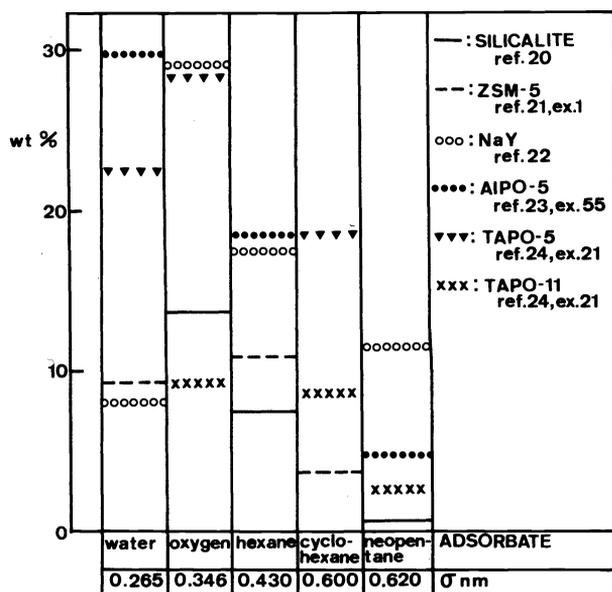


Fig. 1. Sorption of molecules with different kinetic diameters ($\sigma$) over some zeolites and molecular sieves

This information is useful for the catalytic chemist, but the method suffers from the fact that mostly one-point adsorption measurements are made; only when the whole adsorption isotherm is known, the precise value of the sorption capacity can be derived without any interference from capillary condensation phenomena. In fact changes in crystal morphology or the presence of mesopores as in stabilized Y-zeolite (ref.25) may cause distinct sorption differences. Moreover, the whole procedure is time consuming (ref. 26).

## USE OF MODEL REACTIONS

The basic test of a zeolite or molecular sieve for a particular catalytic application will always remain the catalytic reaction. However,it is hardly conceivable that for every new potential catalytic application always a detailed screening procedure should be made. Therefore, a good test reaction should give as much information as possible to establish rules and know-how, which ultimately can be used for the preparation of tailor-made catalysts. It is essential that (a) test reaction(s) inform(s) on the following aspects of the catalyst :

i. effective pore size and architecture of pores and cages, preferentially in working conditions, i.e. at elevated temperatures and/or pressures;

ii. nature of active sites present = Brønsted and Lewis acid sites, acidobasic sites, metallic sites and electric fields and gradients;

iii. concentration of these sites, their repartition in the intracrystalline volume, their presence at the external crystal surface, the existence of concentration gradients across the crystal;

iv. catalytic stability and regenerability.
It is not very probable that a single model reaction can provide all this information. From the work done in the area, it follows that test reactions commonly used are suitable for the characterization of either :
    i. the nature and strength of the acid sites, or
    ii. the intracrystalline void space, or    iii. the catalyst stability.

With respect to (i) a few thousand of contributions appeared in literature. The present contribution will limit itself to (ii), the characterization of the intracrystalline void space of zeolites and molecular sieves using catalytic model reactions. A critical overview of work in this area will be followed by some new significant data.

## MODEL REACTIONS FOR THE CHARACTERIZATION OF THE INTRACRYSTALLINE VOID SPACE OF ZEOLITES AND MOLECULAR SIEVES

### 1. The constraint index

Workers at Mobil Research laboratories in their patent literature have used the so-called constraint index (CI) (ref. 27) to discriminate within the family of acid zeolites. The test relies on the selectivity in catalytic cracking of n-hexane (nC6) and 3-methylpentane (3MC5) in specific conditions. The CI is defined as (ref. 27)= CI = log(fraction nC6 remaining)/log (fraction 3MC5 remaining) and is approximately equal to the ratio of the first order cracking rate constants. This CI has been critically examined recently :

i. mechanistically, paraffins can be cracked either via a classical bimolecular hydride transfer mechanism involving tricoordinated carbenium ions (mechanism A) or via non-classical penta-coordinated carbonium ions (mechanism B) (ref.28). Mechanism A requires a bulky bimolecular transition state while B occurs via a monomolecular step. This has the following implications on CI :
- on large pore zeolites (omega,Y) and silica-alumina, mechanism A dominates. Consequently, the differences in CI between Y and ZSM-5 are the result of pore geometry differences (ref. 28);
- on HZSM-5 it decreases with increasing temperature since B dominates over A at higher reaction temperatures (ref. 28);
- mechanism A for n-C6 and 3MC5 involves secondary and tertiary carbenium ions, respectively; the CI on large pore zeolites will therefore be dependent on the strength of the Brønsted acid sites (ref.29), since tertiary carbocations can be formed on weaker sites than secondary ones.

ii. the presence of 1% of Pt enhances CI on ZSM-5 (ref.30). This is not the result of pore blockage by metal particles, since the activity is enhanced as well. It can result from a change in mechanism in which C6-cations instead of C3-ions intervene, which causes bulkier transition states (ref. 29).

iii. coking of the zeolite may change CI. This has been illustrated for offretite (ref. 29) in which CI grows almost exponentially with time-on-stream. This is explained by a faster coking of the sites in the large channels compared to the smaller ones (ref. 30). In fact, since gmelinite cages (in offretite and erionite) will accept preferentially n-paraffins, the CI in such zeolites is expected to be very high. The high value reported for erionite should be the result of cracking at the external surface of the crystals or pore mouth cracking.

It follows that the rate limiting step of this cracking reaction may change from large to small pore zeolites and the value of CI may be dependent for a given structure on the crystal size, the acid site strength and the Si/Al ratio (ref. 31).

In this way, all zeolites with $1 \leqslant CI \leqslant 12$ are considered to be medium pore zeolites (ref. 33). CI should therefore be used in the context it was developed for: to discriminate between large and medium pore zeolites. Since the reaction mechanism and rate determining step of the cracking reactions may differ from one zeolite to another, the linear relationship found between log (CI) and the pore size (ref. 32) is of no fundamental nature and happens to be accidental. A more satisfactory characterization reaction of the intracrystalline void structure of zeolites would be the conversion of a single reactant into products of different size via competitive decomposition pathways (ref. 3).

### 2. The *m*-xylene conversion reaction

It is not the aim of this work to discuss all the medium pore zeolites, mainly characterized by 10-membered rings (10-MR), used as isomerization catalyst for m-xylene. Only a few papers will be considered in which the conversion of m-xylene intentionally was used as a tool for the characterization of zeolite pores or intracrystalline void volume. The ratio R of the rate constants for o-xylene and p-xylene formation out of m-xylene, respectively, has been proposed as an essential feature of the zeolite structure (ref. 31) :

$$R = \frac{k \text{ (o-xylene from m-xylene)}}{k \text{ (p-xylene from m-xylene)}}$$

It is easily shown that this ratio is proportional to the ratio of the effective diffusion constants for the respective isomers and R becomes a structural parameter independent from the crystallite size and the distibution (ref. 3) and strength of the active sites. All structures which contain acid sites and in which the formation of the 1,2-isomer from the 1,3-isomer is diffusion controlled will be susceptible to characterization by this method. The R value is therefore a good parameter for probing medium pore zeolites. A few relevant data are illustrating these points in Fig. 2.
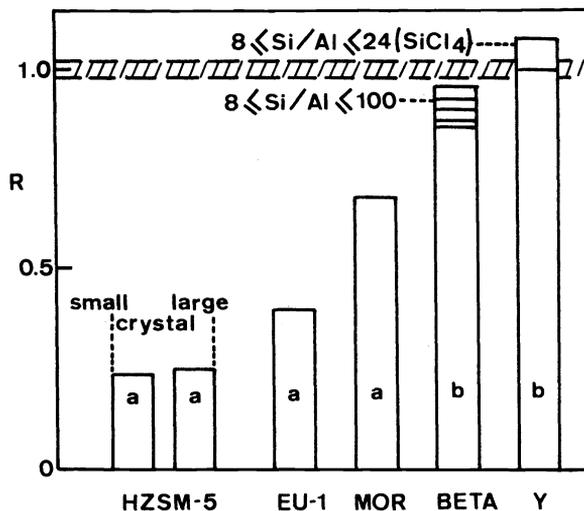


Fig. 2. R values from the isomerization of m-xylene on zeolites at a, 673 K, taken from ref. 31 or b at 623 K from ref. 34; the dashed line represents the thermodynamic constraint (ref.35).

The R value, although not yet systematically determined for different zeolites, seems to cover a wider ringe of pore sizes than CI since mordenite and zeolite BETA can be distinguished from on one hand the medium pore zeolites and on the other hand from the large pore zeolites in which o-xylene rapidly diffuses.

## 3. Ethylbenzene disproportionation

1,3-dimethylbenzene can be transformed directly into a mixture of the three trimethylbenzene isomers by a disproportionation reaction. Since the 1,2,4-, 1,2,3- and 1,3,5- trimethylbenzenes have distinctly different kinetic diameters (ref. 36,37) and the reaction is bimolecular, it follows that selectivity changes will be provoked by both transition state shape selectivity and by changes in the diffusion pathways. The formation of this bimolecular transition state, however, can as well be influenced by geometric constraints in the intracrystalline void volume, as well as by the density of sites. Apparently, the formation of benzenium ions with diphenylmethane skeleton which seem to be intermediates in this reaction, require a pair of sites (ref. 38). A less bulkier transition state is expected to be formed in the isopropylation reaction of benzene. Differences in the p/o ratio of the diisopropylbenzenes reported will therefore reflect mainly differences in the effective diffusion coefficients of the respective isomers. Consequently this reaction is one of the many which if systematically used could discriminate within the group of medium pore size zeolites. It should be stressed that with all these reactions the catalysts should be compared at constant temperature and conversion but also at equal coke content.

Also the disproportionation of ethylbenzene is a valuable candidate for void characterization in zeolites (ref. 40,41) because of the small size of the feed but will suffer from the same shortcomings as all other reactions of this class : distinction between diffusion and shape selectivity is difficult, transition state selectivity will be determined by site density as well as by void size, coking rates will differ with the zeolite and comparison at equal degree of coking will be difficult. Criteria which can be used are :

i, the presence of an induction period, which for unknown reasons only occurs with wide pore zeolites (ref. 41);

Internal ring alkylation to c- or t- decaline is very much structure-dependent (ref. 42,47) and the selectivity in a wide range of temperatures does not change (ref. 42).

The formation of isobutane from n-butylcyclohexane (ref. 48) and indirectly from cyclodecane, occurs via the so-called pairing reaction : via classical bifunctional catalysis the substituents on the cyclohexane/cyclopentane ring are rearranged until a quaternary carbon atom is formed :

**isobutane**                          **n-butane**
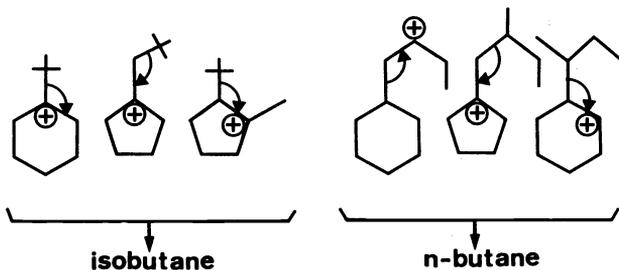
Type A and Bl β-scissions on those bulky intermediates give isobutane (ref. 48). If bulky and energetically preferred (ref. 48) intermediates for steric reasons cannot be formed, the above scheme shows that n-butane is formed via B type β-scissions. High i-/n-butane ratios will therefore always be found if sufficient space is available. Since both hydrocarbons have equal diffusion coefficients in ZSM-5 (ref. 49), this criterion will not be influenced by diffusion effects and therefore by crystal size and morphology of the zeolites unless perhaps in dense zeolite structures. Fig. 3 shows that both ratios are as expected conversion (and temperature) independent even for the large pore zeolite BETA.
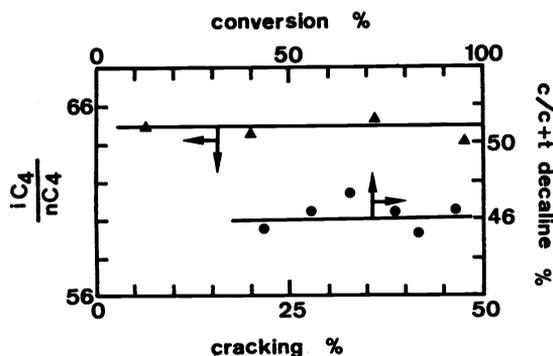


Fig.3. Dependence on the degree of cracking of cyclodecane of two potential void characterization criteria on zeolite Pt/H-BETA (reaction conditions of ref. 42).
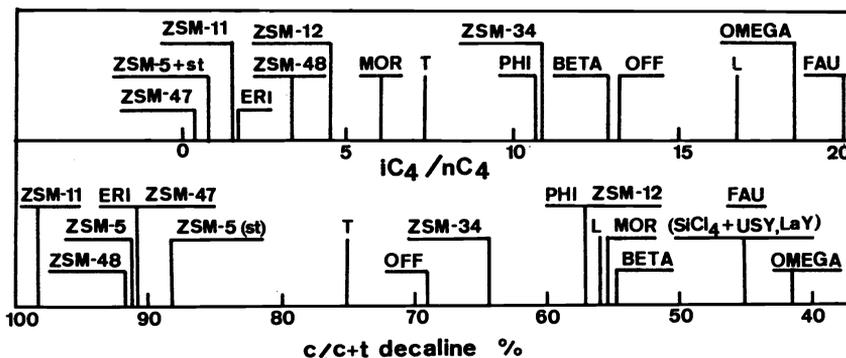


Fig.4. Structural ranking of Pt/H-zeolites with the help of the cyclodecane conversion reaction, using certain product ratios as independent characterization criteria.

This is further substantiated by literature data from butylcyclohexane (ref. 48) and cyclodecane (ref. 42). On different samples of HZSM-5 as well as Y, similar values of this i/n ratio have been obtained using both probe molecules. New data using cyclodecane as feed and quantifying with both criteria are shown in Fig. 4.

ii, the rate of deactivation, which is faster on the large pore zeolites (ref. 41);

iii, the diethylbenzene/ benzene product ratio, which is only near-stoechiometric with the large pore zeolites;

iv, the distribution of the diethylbenzene isomers (ref. 41).

An overview of the significant results taken from this paper are summarized in Table 1. Although the mechanistic consequences of at least 2 parameters remain obscure, it is clear that the simultaneous use of several criteria from a single reaction constitutes a powerful tool in zeolite charaterization. Some criteria may be perturbed by reaction of the external OH groups and as a result of different degrees of coking  at which they are measured. Nevertheless, taking together the information of the 4 criteria, the known structures can be correctly classified in terms of large  pore (12-MR) and medium pore zeolites (10-MR).

TABLE 1. Overview of potential parameters useful in the characterization of zeolites using ethylbenzene disproportionation at 523 K (data from ref. 41)

| criterion | I | II | | III | | IV |
|---|---|---|---|---|---|---|
| Zeolite | Induction period estimation (1) | Degree of deactivation (2) | DEBz/BZ (3) | Distribution of DEBz isomers (%) 1,2 | 1,3 (4) | 1,4 |
| HZSM-22 | 0 | 66 | 0.66 | 1.3(0) | 46.7(37.6) | 52.0(62.4) |
| HZSM-5 | 0 | 71 | 0.75 | 0.0(0) | 57.8(52.6) | 42.2(47.4) |
| HZSM-35 | 0 | 57 | 0.75 | 1.7(1.7) | 58.6(55.7) | 40.0(47.4) |
| HZSM-34 | 0 | 14 | 0.72 | 4.3(2.9) | 60.0(47.7) | 35.7(48.4) |
| HZSM-12 | 15 | 0 | 0.90 | 5.8(5.8) | 62.1(62.1) | 32.1(32.1) |
| HZSM-25 | 0 | 71 | 0.90 | 6.7(6.7) | 62.7(62.7) | 30.9(30.9) |
| HY | 15 | 72 | 0.90 | 5.8(5.8) | 62.1(62.1) | 32.1(32.1) |

1,100x(maximum-initial conversion)/(maximum conversion); 2, 100x(conversion after 2.5 - 20.0 hours on stream)/(conv. at 20.0 hours on stream); 3, diethylbenzene/ benzene product ratio; 4,after 2.5 hours and in brackets after 20 hours on-stream.

## 4. Bifunctional conversion of naphtenes

When bifunctional zeolites, i.e. acid zeolites loaded with not more than 1% by weight of noble metal, are used for catalysis of hydrocarbon reactions, no coke formation occurs on a well-balanced catalyst and no time-on-stream dependence of the selectivity exists. In case of monodimensional small tubular pores, obstruction of some pores by metal clusters may cause the same effects as pore blocking by coke deposition on monofunctional zeolites.

On a qualitative basis, the work reported on bifunctional conversion of naphtenes and alkylaromatics : cyclodecane (ref. 42,43), ethylbenzene-ethylcyclohexane (ref. 44-46), mono-, bi- and tricyclonaphtenes (ref. 47), can be used to distinguish between ZSM-5 and ZSM-11 and consequently within the group of 10-MR zeolites. Unfortunately, the reaction networks are quite complex and since each parameter selected to probe the void volume is to some extent temperature and conversion dependent, it is not yet possible in this way to characterize a 10-MR zeolite in terms of the dimensionality of the pore system. Moreover, it is not yet possible to distinguish without any doubt 10-MR tubular pores from voids consisting of small cages accessible through only 8-MR.
A closer look to these data on cyclodecane (ref. 42,47) and butylcyclohexane (ref. 48) conversion allows to derive two sensitive and quantitative criteria as far as probing of the void space is concerned.  The reaction network of cyclodecane conversion on Pt/H-zeolites can be schematicallly represented as follows :

cyclodecane ⟶ [bifunctional ring contraction] ⟶ ------ + butylcyclohexane
                ⟶ [bifunctional internal ring alkylation] ⟶ c,t-decaline

isobutane ⟵ [bifunctional pairing] ⟵
cyclohexane + butane ⟵ [dealkylation] ⟵
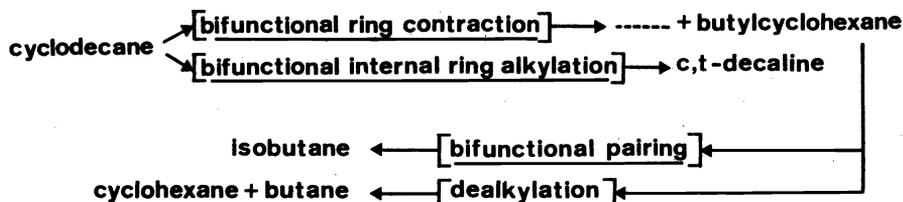
The following striking features emerge from this picture :

i.  both criteria do not rank the same structures in the same way; this has to do with differences in local constraint which are not clear at this moment;

ii. the two criteria have different sensitivities and act complementary : the i/n ratio distinguishes easily within the 12-MR zeolites and is structure but not treatment sensitive for the 10-MR (ZSM-5 and its steamed homologe behave in an identical way).

iii.the decaline ratio is structure sensitive for faujasite, classifies T, OFF and ZSM-34 in a separate group of structures, but distinguishes ZSM-5 from its steamed form.

When these criteria will be determined for all known structures, they will definitely allow to classify zeolites according to their pore size and structure.

## 5. The bifunctional conversion of n-decane

The n-decane hydroconversion has been shown to be a very suitable test reaction which is able (ref. 50) to classify zeolites according to the architecture of their voids. Since n-paraffins are able do diffuse through 10-MR zeolites, this reaction allows to classify zeolite structures in terms of :
   12-MR pores, 12-MR pores with lobes of different sizes, 8-MR windows
   limiting cages of different sizes and 10-MR zeolites.
Five different criteria are used and interpolation of their values within those obtained for known zeolite structures, allows to give a fair prediction of the zeolite pore architecture.  The different criteria constitute as much independent criteria for void volume characterization but show a different sensitivity to changes in pore volume :

1. The relative distibution of the di- and monobranched feed isomers at maximum isomerisation conversion; this is a crude way of making distinctions; the external surface and therefore the crystal morphology possibly disturbs the values.

2. The ethyloctanes yield of the monobranched isomers at 5 % isomerisation conversion is very sensitive since irrespective of crystal morphology, these isomers are never formed on 10-MR zeolites.

3. The ratio of 3- to 4-ethyloctane further distinguishes one structure from the other; criterion 2 and 3  are based on differences in both transition state and diffusion shape selectivity of these isomers.

4. The relative concentration of  2- and 5-methylnonane in the monomethyl branched isomers at 5% isomerization conversion seems less sensitive for 12-MR  zeolites, but reflects structural changes in 10-MR zeolites; this selectivity aspect is most probably transition state controlled (ref. 51). This is  also confirmed by the observation that X-ray amorphous ZSM-5 zeolite (ref. 52) shows the same initial selectivity.

TABLE 2. CI° and CI |ref.33| values of zeolites compared to their void characteristics

| zeolite | CI | CI° (a) | void characteristics | | dimensions/nm |
|---|---|---|---|---|---|
| L | – | 1.0 | 1D | 12MR | 0.71(lobe 0.75) |
| omega | – | 1.2 | 1D | 12MR | 0.74 |
| HY | – | 1.3 | 3D | 12MR | 0,74(cage 1.2) |
| ZSM-3 | – | 1.3 | faujasitic(f) | | |
| BETA | 0.6 | 1.4 | | | |
| PHI | – | 1.4 | | | |
| mordenite | 0.4 | 1.8 | 2D | 12MR | 0.67 x 0.70 |
| | | | | 8MR | 0.57 x 0.29 |
| offretite | 3.7 | 1.8 | 2D | 12MR | 0.64 |
| | | | | 8MR | 0.52 x 0.36 |
| ZSM-25 | | 2.2 | | | |
| ZSM-12 | 2.0 | 2.2 | 1D | 12MR | 0.61 x 0.57(b) |
| chabasite | – | 2.3 | 3D | 8MR | 0.37x0.36(cage 1.10x0.65) |
| alpha | – | 2.4 | 3D | 8MR | 0.41(cage 1.14) |
| erionite | 38 | 2.5 | 3D | 8MR | 0.52x0.36(cage 1.50x0.63) |
| T | – | 2.7 | | | |
| ZSM-47 | – | 2.7 | | | |
| ZSM-11 | 8.7 | 2.7 | 2D | 10MR | 0.55 x 0.51 |
| clinoptilolite | – | 3.6 | 2D | 10MR | 0.72 x 0.44 |
| | | | | 8MR | 0.55 x 0.44 |
| | | | | 8MR | 0.47 x 0.41 |
| ZSM-48 | 5.3 | 5.2 | 1D | 10MR | 0.56 x 0.53(c) |
| ZSM-5 | 8.3 | 6.8 | 2D | 10MR | 0.54 x 0.52 |
| ZSM-35 | 4.5 | 8.1 | | | |
| ferrierite | – | 10.3 | 2D | 10M | 0.55 x 0.43 |
| | | | | 8MR | 0.48 x 0.34 |
| ZSM-23 | 9.1 | 10.8 | 1D | 10MR | 0.56 x 0.45(d) |
| ZSM-22 | 8.2 | 14.4 | 1D | 10MR | 0.55 x 0.45(e) |

a,1D = mono, 2D = bi and 3D = tridimensional; b,ref.53; c, ref.58; d,ref.57; e,ref.58; f,ref. 55.

5.The absolute yield of isopentane formed at 5% hydrocracking conversion also reflects the probability of central β-scission of highly branched and therefore bulky C10 isomers. Using this method the void structure of ZSM-12 : "a 12-MR pore zeolite with pore size between offretite and mordenite" (ref. 50) has been correctly predicted (ref. 53); also ZSM-48 has been correctly classified as a 10-MR zeolite (ref. 50), although the dimensionality of this material could not be predicted. Details on the void structure of zeolites BETA, PHI, ZSM-34, ZSM-47 and T were derived which by any other characterization technique, apart from the mentioned crystallographic methods, cannot be obtained. On the at that time proposed refined contraint index (CI°) (ref. 50) will now be elaborated.

CI° is the ratio of 2- to 5-methylnonane at 5% izomerisation conversion of n-decane. Since bifunctional chain branching occurs via protonated cyclopropane (PCP) intermediates, at low conversions and in absence of geometric constraints CI° is expected to be equal to 1. This value is predicted if equal concentrations of all n-decyl PCP ions and identical transformation rates for them are assumed (ref. 54). It should also be stressed that totally different phenomena are at the origin of the CI° and CI. Pertinent data on void characteristics of zeolites, CI and CI° values are given in Table 2. The zeolites are ranked according to increasing CI°values. It is seen that there exists a very close correlation between CI° and the pore size and structure. Zeolite cages accessible through 8-MR have CI° intermediate between the value for 12-MR and 10-MR zeolites. These intermediate CI° values are apparently determined by a transition state effect (in the cage) and a diffusion effect (through the 8-MR). For the 12-MR zeolites, CI° is less sensitive for the large pore structures (CI° < 1.4). This is caused by a dependence upon the zeolite of the relative rate of the methyl-shift in monobranched isomers compared to the rate of branching. In the 10-MR materials, a very sensitive ranking is possible, mainly of the ferrierite-type materials (ZSM-22,-23,-35 and ferrierite). Although crystallographically the 10-MR pores of ZSM-22 and ZSM-23 are similar except for subtle differences in the pore openings (ref. 57), the CI° values discriminate clearly between those materials. For the 10-MR and 12-MR zeolites for reasons mentioned earlier (transition state selectivity), CI° will be structure specific. Effects of crystal size for obvious reasons are to be expected for zeolites with cages accessible through 8-MR.

## 6. The characterization of molecular sieves with the decane test

The new family of microporous crystalline polyoxides synthesized recently have all more or less pronounced acid activity (ref. 59,61). Therefore, they are susceptible for characterization by the decane test. To illustrate the applicability of the method, AlPO-9 (ref. 23), TAPO-5 and TAPO-11 (ref. 24) with 9% of TiO$_2$ and SAPO-5 and SAPO-11 (ref. 62) with 15% of SiO$_2$ were synthesized according to the patent literature. The Al/P ratio in every case was equal to one. Although the chemical composition for these materials predicts the absence of acidity, for unknown reasons they contain enough residual Brønsted sites to transform them into bifunctional catalysts of medium activity.

TABLE 3. Estimation of void space of molecular sieves according to CI°

| type | CI° | pore size° | largest molecule adsorbed (nm) | | ref. |
|------|-----|-----------|----------------------|---|-----|
| SAPO-11 | 3.6 | 10-MR | cyclohexane | 0.6 | 62 |
| SAPO-5 | 1.5 | 12-MR | neopentane | 0.62 | 62 |
| AlPO-9 | 1.8 | 12-MR | | | 23 |
| TAPO-5 | 2.2 | 12-MR or 8-MR (cages) | cyclohexane | 0.6 | 24 |
| TAPO-11 | 3.3 | 10-MR | cyclohexane | 0.6 | 24 |

Consequently, they are susceptible to characterization with the n-decane test. CI° values are shown in Table 3. According to this criterion SAPO-11 and TAPO-11 have effective pore sizes comparable to the 10-MR zeolites. SAPO-5, AlPO-9 and TAPO-5 are 12-MR molecular sieves (MS). In Fig.5, the ethyloctane criterion is illustrated for the same MS. SAPO-11 and TAPO-11 are again classified as 10-MR materials. It should be checked whether the formation of small amounts of ethyloctanes on TAPO-11 occurs at the external surface or is the result of heteroatom substitution (ref. 63). This criterion classifies AlPO-9 and SAPO-5 as 12-MR materials with similar effective pore sizes. For TAPO-5 the use of only 2 criteria does not allow to distinguish 12-MR pores from a structure with cages accessible through 8-MR.

## 7. Paraffin cracking

When C$_6^+$ paraffins are cracked, it was shown recently that C4/C3 or C4/C2 ratios of the cracked products changed with the zeolite structure (ref. 64). Low C4/C3 ratios are typical for small pores or cages accessible through 8-MR. Although mechanistically, the situation is not entirely clear, the reaction seems to be useful"for the prediction of the presence of small cages or channels in an unknown zeolite structure" (ref.64).
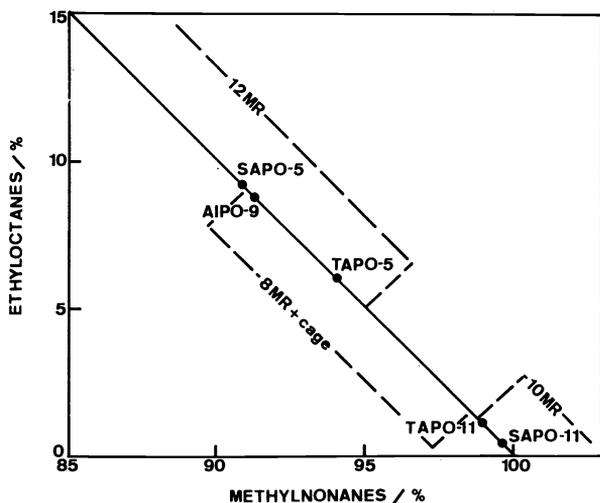
Fig.5. Illustration of the ethyloctanes formation in the monobranched isomers from n-decane hydroconversion over representative molecular sieves. The frame of the figure was obtained for zeolites (ref.50).

## CONCLUSIONS

The present literature overview demonstrates clearly that the systematic application of some chemical test reactions can be used to characterize the pore sizes of zeolites and molecular sieves. For relatively complex reactions sometimes several independent criteria can be used to classify known zeolites. Through interpolation, the void architecture of unknown zolites or molecular sieves can be characterized in more detail. The hydroconversion of n-decane is such a promising test, although others (cyclodecane or butylcyclohexane hydroconversion) seem to be very useful as well.

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