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Standard reaction tests for microporous catalysts characterisation

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Abstract

The distribution of reaction products in properly chosen simple test reactions, exploiting the acidic properties of the catalyst, allows to define the value of some characteristic parameters, such as the constraint index (CI), the modified constraint index (CI*) and the spaciousness index (SI), tightly correlated to the structure of zeolite-type microporous catalysts. This permits to clearly distinguish the behaviour of small-, medium- and large-pore microporous materials, the pore diameter of which can be easily ranked on the basis of a very few or even of only one test reaction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Molecular sieves microporisity; Microporous catalysts; Standard reactions

1. Introduction

The choice of molecular sieves as dimensionally selective catalysts requires an as rapid as possible collection of reliable information on the porous structure of such materials. This information can be obtained from either crystalline structure or selectivity in adsorption of properly selected probe molecules or selectivity to some products in properly chosen test reactions [1]. For example, X-ray diffraction (XRD) has become one of the most widely employed techniques for analysing crystal structure [2–5], for determining the degree of crystallinity, phase purity and crystal symmetry. Additional information can be obtained by scanning electron microscopy (SEM), neutron diffraction, high resolution electron microscopy (HREM) and magic-angle spinning nuclear magnetic resonance (MAS-NMR). However, all of these methods require expensive special instruments and they are often time-consuming, an important disadvantage for routine application. The adsorption of molecules of progressively increasing size, such as O_2, H_2O and hydrocarbons, has been also proposed [6]. However, this technique can be safely applied only on catalytically inactive molecular sieves or at subcatalytic temperature.

On the other hand, the use of catalytic probes is very rapid, it does not require any expensive apparatus and allows to test the catalyst under its usual reaction conditions. Hence it has become increasingly popular and in recent years several reactions have been proposed and employed routinely, especially for zeolite-based catalysts [1,7–13].

2. The microporous systems in zeolites

Zeolitic catalysts are characterised by small and uniform pores. The active sites being located mainly

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within the pores, the probability for reactants to penetrate inside the pores and react depends on pore size and on the structure of reacting molecule. Indeed, only the molecules smaller than the pores can react and only the molecules that are able to diffuse out of the pores appear as products. Therefore, several different types of selectivity have been defined and generally accepted (Fig. 1):

(i) *Reactant selectivity*, when only sufficiently small reacting molecules can diffuse inside the catalyst pores and so transform into products. An example is the selective cracking of linear, with respect to branched paraffins in zeolite A (Fig. 1(a)).

(ii) *Product selectivity*, when only sufficiently small product molecules can diffuse outside the pores. In this case larger molecules forming inside the pores are converted into sufficiently small molecules, e.g. through an equilibrium reaction, so to diffuse outside, or they are transformed into polymers or coke, ending in catalyst deactivation. An example is the alkylation of toluene with methanol on ZSM5 zeolites. The selectivity to the p-isomer is enhanced, due to its three orders of magnitude larger diffusivity, with respect to the o- and m-isomers (Fig. 1(b)).

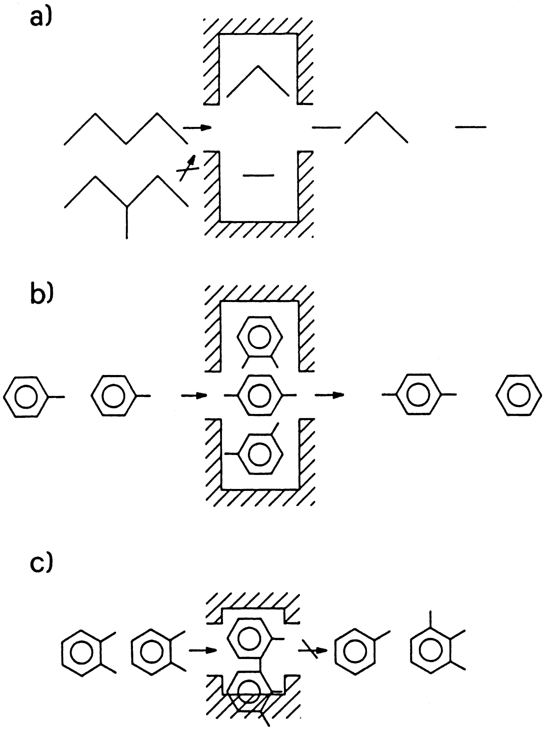

Fig. 1. Examples of (a) reactant selectivity, (b) product selectivity and (c) restricted transition-state selectivity.

(iii) *Reaction intermediate selectivity*, when, though reactants and products can diffuse freely within the pores, some reactions are hindered, because the size of the corresponding reaction intermediate is larger than the room available within the pores. An example is the bimolecular transalkylation reaction of dimethylbenzenes, in which the formation of the 1,3,5-isomer is hindered, due to the size of the reaction intermediate, which overcomes the pore diameter (Fig. 1(c)).

From this point of view alkylation reactions are very interesting, because the nature of the products formed indicates which of the possible intermediates are favoured, so allowing to characterise the catalyst. Another example is the alkylation of toluene with methanol on Na-X and Cs-X zeolites (Fig. 2). The smaller size of Na^+ cations leads to the equilibrium mixture of o-, m- and p-xylene, while the presence of the cumbersome Cs^+ ions favours the alkylation on the side chain, leading prevalently to a mixture of ethylbenzene and styrene.

(iv) *Molecular traffic control selectivity*, in zeolites possessing a bi- or pluri-modal porous system [14]. In this case the reactant can diffuse inside preferentially through a given type of pores and the product diffuses outside through another type of pores, according to their molecular size. In some cases this can minimise the effect of counterdiffusion, so enhancing the reaction rate.

3. Standard reaction tests

The various kinds of selectivity can be distinguished experimentally. For instance, reactants and products selectivity is controlled by mass transfer inside the pores and hence by the crystal size of the catalyst, while reaction intermediate selectivity is unaffected by such a parameter. Furthermore, to get information on the pore structure of a catalyst it suffices to compare its selectivity in a given set of probe-reactions with that measured on known catalysts for the same reactions. This approach was proposed originally by Frilette et al. [7], who compared the cracking of an equimolar mixture of n-hexane (nH) and 3-methyl-pentane (3MP) on acidic zeolites. They

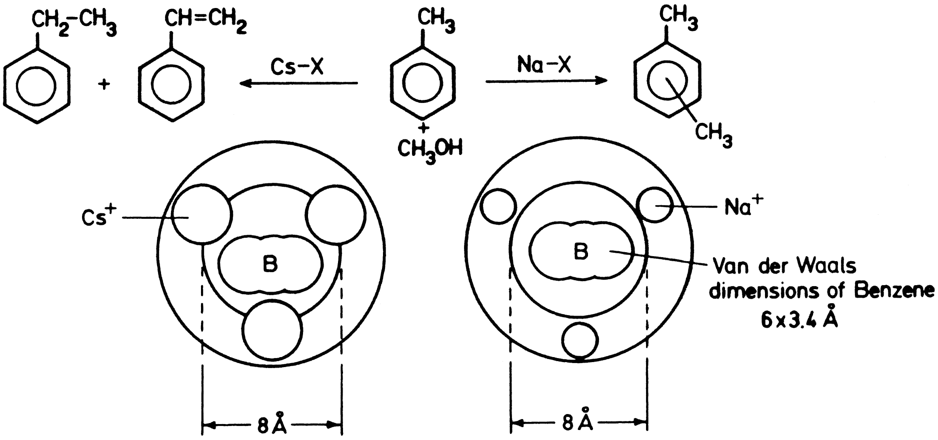

Fig. 2. Alkylation of toluene with methanol on Cs-X and Na-X zeolites.

noticed that the cracking rate of the two paraffins is affected by the steric hindrance of the reaction intermediate (Fig. 3). Furthermore, at a given temperature and for a given strength of acid sites, the ratio of pseudo-first order cracking rates ($k_{n\mathrm{H}}/k_{3\mathrm{MP}}$), referred to as constraint index (CI), grows with decreasing pore diameter and in the presence of small amounts of noble metals in the catalyst.

Later on, other probe-reactions, catalysed by Brønsted (B) acid sites, were proposed. One of them, useful for characterising the pore structure of zeolitic catalysts, is the conversion of *m*-xylene to *o*-+*p*-xylene [6,7]. The characteristic parameter in this case is referred to as the ratio R ($=k_{m\rightarrow o}/k_{m\rightarrow p}$) of the rate of formation of the two isomers. It has been shown that R is proportional to the effective diffusion coefficient of the two isomers, so as to be a structural parameter, independent of crystal size, but depending on the distribution and strength of the B acid sites. This probe-reaction is then useful for all the catalysts in which the formation of the *o*-isomer is controlled by diffusion. R is a particularly good parameter for analysing medium-pore zeolites, covering a larger dimensional field, with respect to CI. The disproportionation of ethylbenzene has also been applied [9], thanks to the relatively small size of the reactant. However, as for all the reactions of this type, it is rather difficult to distinguish between diffusional and dimensional selectivity. Indeed, selectivity is determined by both sites density and pore size. Some further independent criteria can however be of help, such as the length of induction period, the rate of coking, the yield ratio of diethylbenzene (DEB) over benzene and the distribution of DEB isomers. Another probe-reaction proposed is the transalkylation–isomerisation of 1-methyl-2-ethyl-benzene (1M2EB) [12,13]. The most interesting information one can get from such a reaction concerns: (i) the minimum pore size, from the size of reaction products; (ii) the room available around acid sites, from the molecular symmetry of the trialkylbenzenes formed; (iii) the strength of acid sites, from the transalkylation/transmethylation ratio [15]. A specific parameter must be employed for every determination. Of course, some

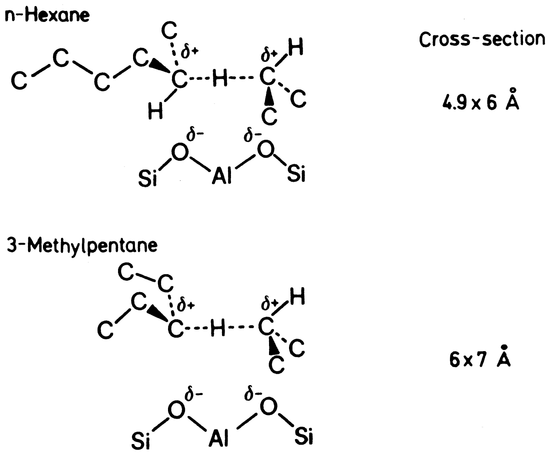

Fig. 3. Dimensions of reaction intermediates of C_6 paraffins.

important limits affect this catalytic test, concerning e.g. the simultaneous presence of catalytically inactive B sites, together with the active ones. Furthermore, the test cannot be applied to zeolites with pore size smaller than 5 Å, due to the relatively large size of the reactant.

4. Bifunctional catalysts

More recently other hydrocarbon reactions over bifunctional catalysts have been considered, particularly the isomerisation and hydrocracking of long-chain alkanes [8,16] and of C_8–C_{11} naphthenes [10,17–19]. When acidic zeolites, loaded with less than 1 wt% of the noble metal, are employed for catalysing hydrocarbon reactions, the formation of coke is virtually suppressed and hence selectivity becomes independent of time-on-stream. However, with small-pore zeolites, the presence of noble metal particles can have an obstruction effect, similar to that of coke on multifunctional zeolites. For qualitative purposes, the bifunctional conversion of naphthenes and alkylaromatics, such as cyclodecane, ethylbenzene, ethylcyclohexane, mono-, bi- and tri-cyclonaphthenes, can be used for testing ZSM5 and ZSM11, i.e. ten-membered-ring (10-MR) zeolites. Unfortunately, the reaction is very complex and every parameter depends on temperature and conversion, so that the dimensions of the pore system of 10-MR zeolites cannot be characterised reliably. A more interesting probe-reaction is the bifunctional conversion of decane, allowing to classify the pore voidage of zeolites in terms of pore size (e.g. 10-MR and 12-MR) and of pore structure, such as 8-MR windows and 12-MR windows, cages and supercages. Five independent criteria were originally proposed for characterising the catalysts of unknown structure, by comparison with the same parameters, measured on known zeolites. These criteria showed however different sensitivity to change in pore size. From such studies [8] a modified constraint index, referred to as CI^*, has been proposed, defined as the (2-methyl-nonane/5-methyl-nonane) yield ratio, obtained in the isomerisation of decane at low (<5%) conversion. The phenomena determining the value of CI and CI^* are completely different. A real correlation exists between CI^* and pore structure. The structural sensitivity of CI^* is independent of the experimental conditions. Furthermore, the value of CI^* changes with the load of noble metal (e.g. Pt). If Pt wt% is too high, CI^* decreases and hence the sensitivity of such a parameter with respect to the actual pore size of the catalyst becomes lower at higher Pt loading, due to the progressive shifting from intracrystalline to usual metal catalysis over extra-zeolitic Pt. CI^*, as well as the other parameters in the reaction of decane, decreases significantly with decreasing crystal size and with increasing the Si/Al ratio. After an extended study on C_9–C_{11} naphthenes [19], the cracking of butyl-cyclohexane (BCH) has then been proposed as one of the most reliable test reactions for characterising pore volume and structure, especially for larger pore zeolites. Particularly, it was observed that the (iso-butane/*n*-butane) yield ratio, very easily measurable, grows with increasing the pore size of the catalyst. Such a ratio has been referred to as spaciousness index (SI). It has been proven [10] that SI is virtually independent of reaction conditions severity and that it is a particularly sensitive parameter for analysing the pore size typical of 12-MR zeolites. Indeed, in the absence of spatial restrictions, hydrocracking of C10 naphthenes is very selective.

The main products are iso-butane and methyl-cyclopentane [20,21]. The nature of C10 naphthene (BCH, butyl-cyclopentane, etc.) does not affect the selectivity. These unique characteristics are now well known from the mechanistic point of view. The sequence of reaction steps are the following: (i) a ionic β-splitting of the C–C bond takes place first, followed by successive skeletal isomerisations, including widening and narrowing of the annulus; (ii) this mechanism involves only 5- and 6-atom rings, 3- and 4-atoms rings being excluded, due to their too high ring tension; (iii) the C–C bond breaking takes place prevalently, or even exclusively, on the side chain, since the β-splitting of the naphthenic ring is very slow, likely because of the unfavouring orientation of the transition state orbitals [22,23]. The rapid skeletal isomerisation proceeds until a structure forms, allowing a β-splitting of the so-called A-type in the side chain. The main characteristics of this β-splitting is that it starts from and ends to a tertiary carbenium ion [24]. For C_{10} cycloalkyl carbenium ions, three A-type exocyclic β-splitting are possible (Fig. 4).

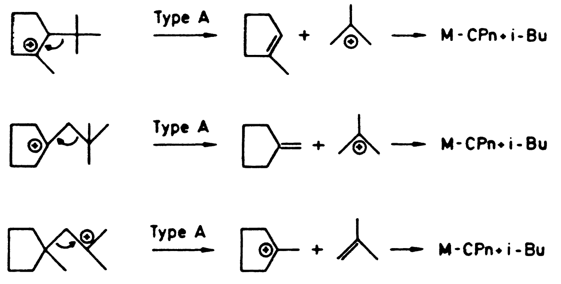

Fig. 4. A-type possible β-splittings of C_{10} cycloalkyl carbenium ions (reprinted with kind permission from [25]).

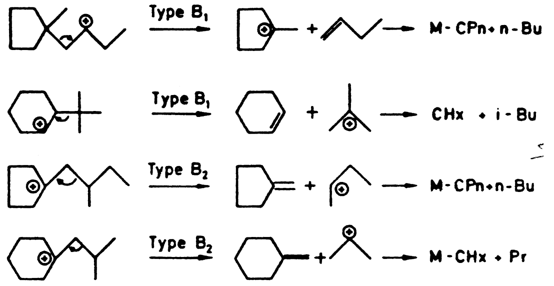

Fig. 5. B-type β-splittings of C_{10} cycloalkyl carbenium ions (reprinted with kind permission from [25]).

One may notice that all of the three lead to methyl-cyclopentane and iso-butane. This gives account of the selectivity observed with bifunctional non-zeolitic and with large-pore zeolitic catalysts such as Pd/LaY [19]. The precursor ions of the A-type β-splitting are relatively cumbersome. If hydrocracking is carried out under steric restriction conditions, the formation of such ions is hindered and the mechanism is referred to as B-type β-splitting. The latter originates from a secondary carbocation and ends to a tertiary carbocation (B1-type) or vice versa (B2-type). Some examples are given in Fig. 5. It is important to notice that now a wider spectrum of products can form, such as *n*-butane, cyclohexane and methyl-cyclohexane, besides iso-butane and methyl-cyclopentane. This has been confirmed experimentally by employing medium-pore zeolites such as Pd/HZSM5 [19]. The detailed analysis of the selectivity of C_{10} naphthenes hydrocracking shows that SI is a particularly useful index for characterising the effective pore size of the catalyst. This index grows from ca. 0.8 for ZSM5, up to ca. 20 for Y-zeolite. Let us consider e.g. the distribution of BCH hydrocracking products [25] over Y-zeolite, Mordenite and ZSM5 (Fig. 6). The results with Pd/HY

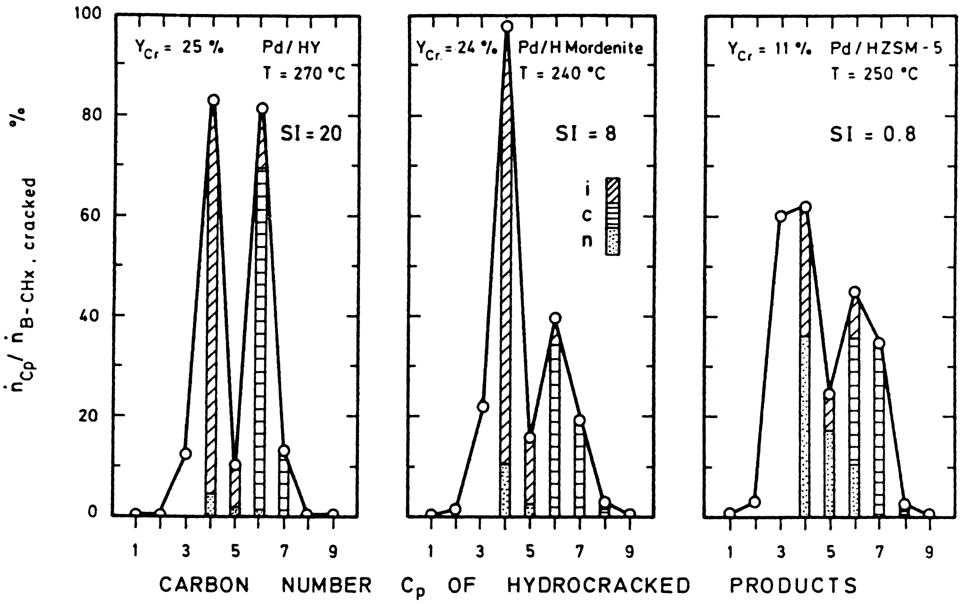

Fig. 6. Selectivity of BCH cracking over Pd/HY, Pd/Mordenite and Pd/ZSM5. *i*, *c* and *n* are the iso, cyclo and normal alkanes, respectively. Y_{cr}=fractional conversion; n_{cp}, n_{BCH_x}=mol of cracked products formed and of BCH consumed, respectively (reprinted with kind permission from [25]).

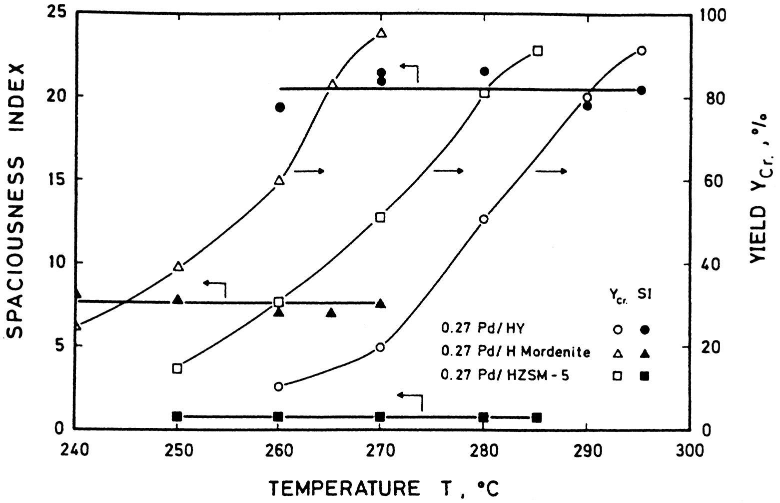

Fig. 7. Effect of temperature on yield of cracked product and on SI of Y-zeolite, Mordenite and ZSM5 (reprinted with kind permission from [25]).

zeolite are similar to those obtained with non-zeolitic catalysts.

The products distribution curve is symmetric for iso-alkanes and cycloalkanes prevailing within the C_4–C_5 and C_6–C_7 fraction, respectively. It may be concluded that no steric restriction is present, the Y-zeolite possessing sufficiently large pores. When employing smaller-pore zeolites such as mordenite and ZSM5, the product distribution is markedly different. The distribution curves are asymmetrical, indicating a noticeable contribution of secondary cracking. The composition of the various C_i fractions changes with decreasing the pore size. Both the abundance of C_3 and the selectivity to *n*-alkanes in higher fractions progressively grow with decreasing catalyst pore size. This is due to the progressive shifting of cracking mechanism from pure A-type β-splitting in Y-zeolite, to a mixed A- and B-type mechanism in Mordenite, to practically pure B-type β-splitting in ZSM5. Furthermore, it has been repeatedly shown [10,11,26] that SI, unlike CI, is independent of reaction temperature. This can be clearly seen in Fig. 7 [25], where the value of SI, determined for the three previously mentioned zeolites, remains unchanged

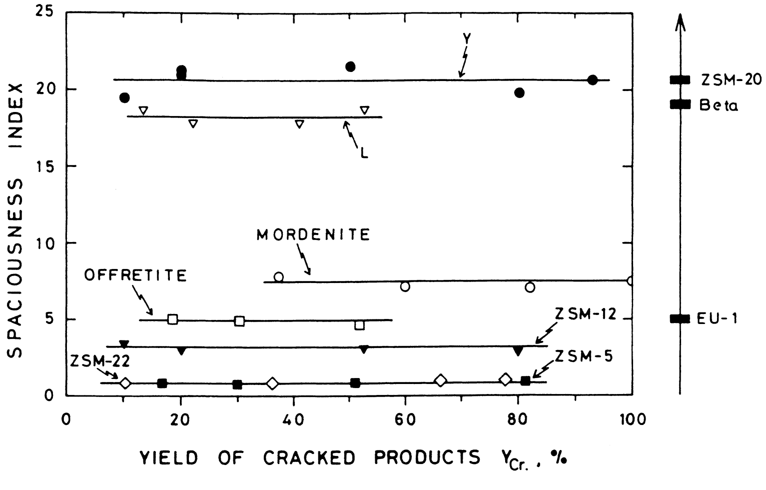

Fig. 8. SI for some zeolites (reprinted with kind permission from [11]).

when temperature, and hence the yield to the various products changes. This is so for every zeolite, allowing to characterise the effective pore size of such materials by means of only one experimental determination at only one temperature. Unlike several chemical reactions, for which selectivity to the various products depends on conversion, in catalytic cracking of BCH, SI is independent of such a parameter (Fig. 8) [11].

This indicates that both iso-butane and *n*-butane do not isomerise under the reaction conditions useful for determining the value of SI. This happens because these species isomerise very slowly towards the equilibrium composition (55% iso- and 45% *n*-butane), the C_4 carbenium ions possesses a too small molecule to undergo any transformation through protonated C_3 intermediates. As for the nature of noble metal in the bifunctional catalyst, it has been noticed that Pt possesses a rather high activity for hydrogenolysis. This means that there exists a real risk that BCH can undergo such a reaction, leading to cyclohexane+*n*-butane. Hence, for routine analysis, the less active Pd is preferred at low concentration. Indeed, also a high Pd loading can lead to a decrease of SI due to hydrogenolysis, as shown e.g. in Table 1.

Furthermore, by analysing a series of 0.27 wt% Pd/ZSM12 zeolites, with SiO_2/Al_2O_3 ratio ranging from 70 up to 300, it has been found that SI grows with such a ratio, but very slowly [25]. It was concluded that SI is virtually independent of SiO_2/Al_2O_3 ratio. Moreover, it was also shown that the distribution of reaction products is practically independent of the zeolite crystal size. This means that intracrystalline diffusion effects are absent and confirms that the value of SI is determined essentially by the size of the reaction transition intermediate, as deduced from mechanistic considerations.

Table 1
Si of H-EU1 zeolite loaded with different amounts of Pd or Pt (reaction temperature 280°C, BCH conversion=30–70% [25])

Metal	Pd			Pt	
wt%	0.05	0.27	2.0	0.5	1.0
SI	6.6	6.0	5.9	4.0	2.8

Fig. 9 summarises the values of CI, CI* and SI determined for some different zeolites [11]. One can observe that medium-pore zeolites (ZSM5, ZSM22) possess SI values slightly lower than 1, though it is well known that the effective pore size of two such zeolites is significantly different. Hence, SI seems unsuitable for analysing the pore size typical of 10-MR zeolites.

For such materials CI* seems by far a more sensitive parameter. For open structures CI* ranges from ca. 1,

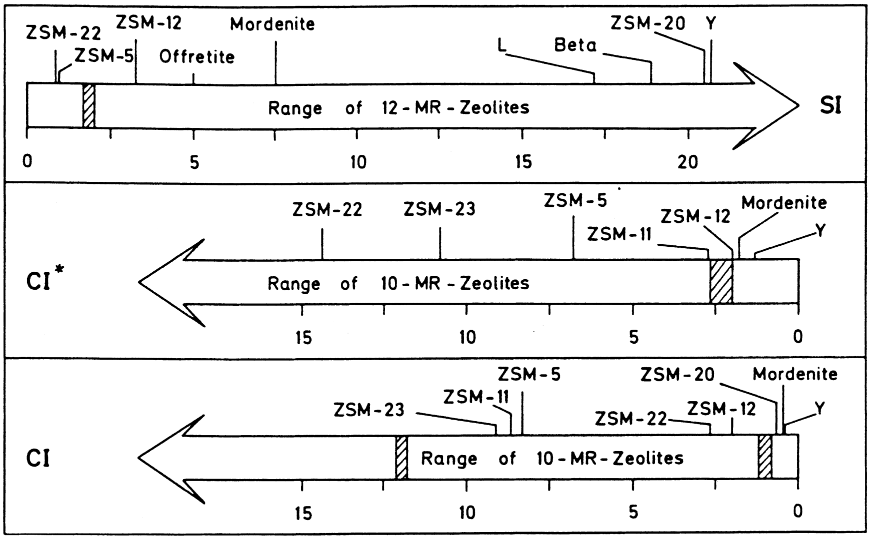

Fig. 9. CI, CI* and SI of some zeolites (reprinted with kind permission from [11]).

typical of pure isomerisation through the cyclopropane ring intermediate, in the total absence of geometric restriction, to 2.2, corresponding to the thermodynamic equilibrium of products distribution. 10-MR zeolites are well analysed by such a parameter, which is able to distinguish neatly between ZSM22 and ZSM23, two zeolites with very similar crystal structure. For 8-MR zeolites, CI^* lies between the values for 10-MR and 12-MR zeolites. This is due to the restriction connected with the different diffusivity of the various methyl-nonanes through the small pores of these materials, superimposing to the restriction caused by the size of the reaction transition intermediate. As a consequence, the size of zeolite crystals may also affect considerably the value of CI^*.

On the other hand, SI is more sensitive for 12-MR zeolites, as mentioned, being able to distinguish between systems characterised by strongly wrinkled pores (ZSM12) and very open structures (Y-zeolite and ZSM20). The high sensitivity of this probe reaction for a given range of pore size is essentially due to the matching of pore size with the size of the reaction transition intermediate.

At last CI seems affected by a larger number of drawbacks, being unable to clearly distinguish the characteristics of many zeolites, both in small- and in large-pore systems. This is the reason why it is less applied with respect to CI^* and SI. The latter, particularly, has gained a wider popularity for medium- and large-pored materials, due to the quick and easy application.

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