Catalysis Letters 22 (1993) 107–121

Adaptation of the porosity of zeolites for shape selective reactions

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The selectivity of zeolite catalysts can be adjusted by modifying the characteristics of the active sites, and by modifying the diffusion path of the reactants and products, as well as the space available around the active sites. In this context shape selectivity, in its multiple aspects, and the most important parameters that influence it, will be discussed. Some examples of selectivity improvement by modification of the zeolite porosity – in particular grafting or deposition of various compounds on the outer surface of the crystallite – are given.

Keywords: Zeolites; shape selectivity; porosity modifications

1. Introduction

Zeolites are crystalline silicoaluminates with a very well defined pore structure, which have a wide range of applications in such varied domains as adsorption, ion exchange and, with particular importance, catalysis.

As catalysts they are best known for their application in catalytic cracking, a process that presents itself as the largest world-wide consumer of solid catalysts, but their applications go well into very diverse areas. Even outside the traditional applications in the field of petroleum refining and petrochemistry, the potential of zeolites as acidic, basic and multifunctional catalysts is, as yet, mostly unexplored.

These catalysts present several distinct properties that enable them to take part in a large series of reactions and processes. Since these solids are well-known superacids, their applications lie mostly in the field of acidic catalysis, having the big advantage, over traditional liquid phase superacids, that they can be easily manipulated and decrease in a drastic way all the problems related to corrosion and pollution that are associated with the latter.

The catalytic properties of zeolites have the specific characteristic, associated with the fact that they are microporous solids. These properties are simultaneously controlled, not only by the properties of the active sites themselves but also by the way these sites are situated inside the microporous structure of the zeolite. This dependency on structural factors can still be conceptually divided into two aspects, one of them being the diffusional path that the molecules (both reactants and products) have to tread on their way from the fluid phase to the active site, and the other being the space available in the vicinity of the acid site itself and which will condition the intermediate steps of the surface reaction.

The greatest potential of these catalysts resides, in fact, in their enormous flexibility, since the main factors regulating the catalytic properties of zeolites (see fig. 1) can be tuned with a reasonable degree of precision through several mechanisms.

The *acidic properties* can be controlled by the adequate choice of the zeolitic structure to be used (there is a large number of available structures) and, within the same structure, by the selection of the parameters that control the strength and distribution of acid sites, namely the Si / Al ratio (by controlling the synthesis conditions or by performing dealumination and realumination treatments) and the nature and quantity of the compensation cations (by resorting to ion exchange techniques).

One must still point out that the advantage given by the possibility of choosing a particular structure can be further enhanced if one takes into account the widening of the composition gamut currently available. The new so-called zeolitic materials are not true zeolites, with the existence of forms having a widely different composition in relation to the classical silicoaluminates, such as AlPOs, SAPOs, or MeAPOs, etc.

The choice of the *geometrical properties* of the zeolite has also to do with structure, and there is a considerable range of pore sizes and types of porous network. The size of the pores can be chosen from large pore zeolites, like zeolite Y and ZSM-20, which are very useful in the transformation of large molecules, to intermediate pore zeolites, like ZSM-5, which already presents shape selectivity towards molecules such as ramified paraffins, down to small pore zeolites that have large applications in the separation of very small molecules, like oxygen and nitrogen (see fig. 2).

The keyword in this paper is *shape selectivity*. This concept emerged in zeolite

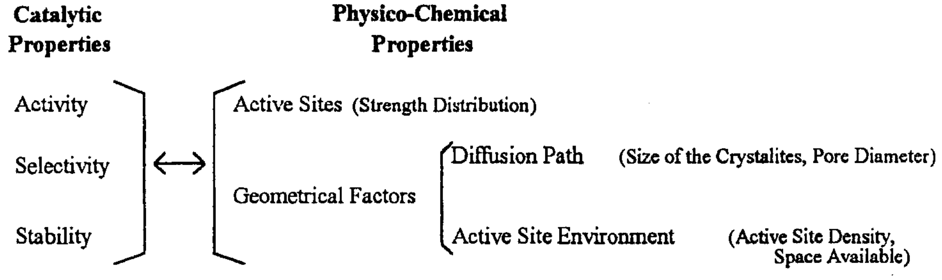

Fig. 1. Schematic representation of the main physico-chemical factors that influence the catalytic properties of zeolites.

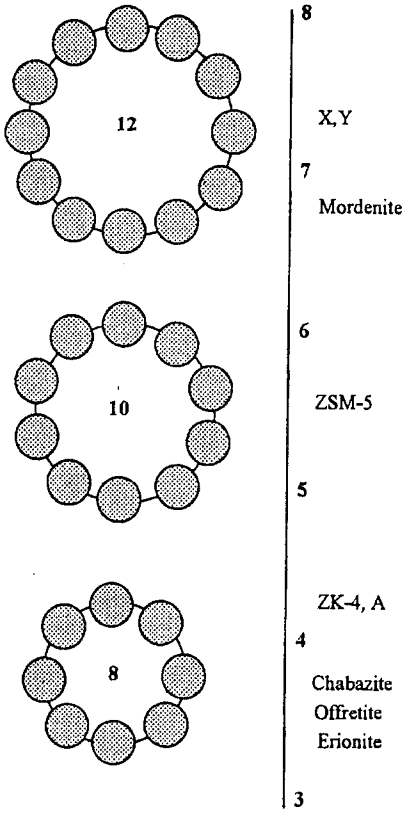

Fig. 2. Dimensions of the pores of different zeolites (in Å).

catalysis as a result of the unique properties that, as we have seen before, make it possible to change the inherent activity of the catalytic sites that exist inside the pores of the solid, by the geometrical characteristics of the crystal network [1]. These effects are mainly due to restrictions, of a geometrical nature, imposed by the dimensions and shape of the pores and cavities of the zeolite. These can assume several different aspects, according to the step where the shape selectivity effect takes place, either during the transport of the reactants and products through the channels of the crystalline network, or during the surface reaction phases [2–10].

2. Different types of shape selectivity

All the processes involving heterogeneous catalysis occur in a sequence of steps that take the reactants from the bulk of the reaction mixture, through the porous structure of the catalyst, right to the active site. At the active site the steps involving the adsorption of the reactant, surface reaction and desorption of the product take place. The product must then take the reverse route until it reaches the reaction mixture again.

Any of the steps occurring inside the zeolite may give rise to different types of shape selectivity, and the main types to be distinguished are the ones involving some kind of restriction on the diffusional path and the ones involving constraints during the surface reaction steps (fig. 3).

The *first type of shape selectivity* is related to the ease with which the species involved in the reaction mechanism can diffuse inside the structure. Selectivity, in this case, will always be obtained at the expense of very strong diffusional limitations relatively to the species to be excluded and the decrease of the global activity will always be observed as a side effect. These limitations can be imposed on the reactants, allowing for the selective transformation of certain species as in *selectoforming*, as well as on the products, allowing the selection, with more or less efficiency, of the desired compounds from a certain range of possible products. In this case the typical example is toluene disproportionation, where the products (xylenes) have different sizes, resulting in the possibility of obtaining selectively the *para* isomer, which has a smaller size, due to the relative ease with which this compound moves in the intra-crystalline space, the channels of the porous network of the zeolite (see fig. 4).

To control this type of selectivity it is necessary to change the opening or the length of the pores of the catalyst. The length of the pores can be changed during synthesis, by controlling the size of the crystallites – the bigger the crystallites are, the larger the shape selectivity effect presented by the zeolite. The changing of the pore openings is limited by the available structures. Small deviations relative to these base dimensions occur due to the specific shape of these channels and to some degree of elasticity shown by these rings [11]. To broaden the available range of pore sizes, it is possible to perform certain post-synthesis treatments, such as dealumination or salt deposition [12], which increase or decrease the pore size, as we

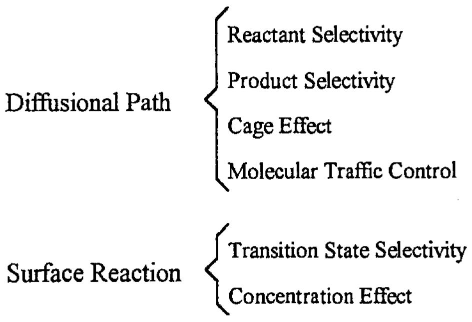

Fig. 3. Main types of shape selectivity, according to the mechanistic step where their action takes place.

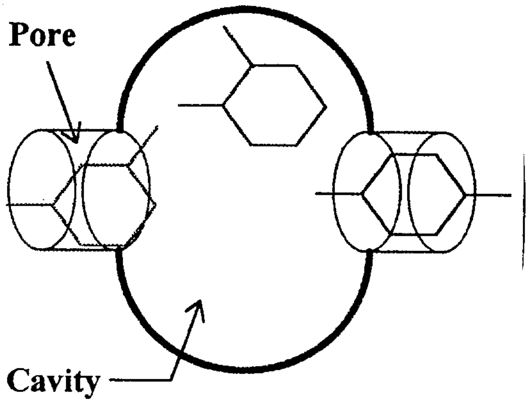

Fig. 4. Shape selectivity effect by diffusional limitations to the transport of products in the reaction of toluene disproportionation.

shall see in the continuation of this paper.

The porous structure has still some other ways of influencing the diffusion of the molecules in its interior, namely through the cage effect and by molecular traffic control. The cage effect is mainly important in linear molecules whose diffusivity does not decrease monotonously with the length of the molecule. The molecular traffic control effect may be important in zeolites having sets of channels with different dimensions, such as ZSM-5. In this case it is possible that the movement of small molecules be restricted mainly to the smaller channels, where large molecules cannot circulate, while the larger channels will be reserved for these latter molecules.

Some other side effects resulting from electrical gradients and the curvature of the surface [13,14], may still significantly influence the selectivity in the case of molecules with different polarizability, as it is likely that these effects will become more and more important as the range of zeolite applications is widened, namely in the fields of fine chemistry and organic synthesis.

3. Methods to modify the porosity

There are a large variety of methods to change the strength and the nature of the active sites of zeolites, and it is also desirable that one develops a set of techniques that allow the modification of the porous structure of the catalyst so that all the catalytic properties of the zeolite may be changed at will.

Changing the operating conditions during the synthesis one may alter the size of the crystallites, with the consequent change in the total length of the diffusional path and also the change of the shape selectivity effects that are introduced by the internal diffusional limitations.

The post-synthesis modification methods can include changes that are either internal to the porous structure of the zeolite, or external, affecting only the surface and the pore openings [15]. These modifications may be achieved by:

– a change in the pore openings by deposition of various materials (either organic or inorganic), with the encompassing decrease of the pore mouth and surface passivation;

– introduction of bulky compounds inside the zeolite's cavities with the aim of restricting the available space in the vicinity of the active site and, thus, affecting the selectivity induced by constraints upon the transition state. Usually it is performed by ion exchange, pre-adsorption of polar molecules or by the use of phosphoric acid, silanes and boranes.

Although the typical application of each of the preceding methods leads to the aforementioned effects, it is not always easy to distinguish between the two ways of action, depending on the zeolite, on the size of the modifying compound, as well as on the operating conditions themselves. In table 1 a comparison between the typical dimensions of one of the most commonly used zeolites in shape selective processes and some of the modifying agents is shown.

It is also interesting that, according to the type and efficiency of the method used, one may simultaneously obtain a change in the strength and nature of the active sites present in the structure, including changes in the acidity and the possibility of preparing multifunctional catalysts, in the case where the modifying agent is not inert in relation to the desired reactions.

We will now refer to each of these techniques separately, giving a few suggestive examples.

3.1. INFLUENCE OF THE ZEOLITE

The first factor to affect shape selectivity is the zeolite itself. This has been studied by many authors, and, as an example, we can see in fig. 5 the influence of the

Table 1
Comparison between the dimensions of the pores of ZSM-5 and some of the most important modifying agents

	Dimensions (Å)	Morphology
HZSM-5	5.4 × 5.6	circular channels
	5.1 × 5.7	elliptic channels
$SiCl_4$	7.6	tetrahedral
$Si(OCH_3)_4$	8.9 ± 0.2	tetrahedral
$ZnCl_2$	7.7 (max.)	linear
	3.6 (min.)	
$GaCl_3$	7.51	dimer (Ga_2Cl_6)
$GeCl_4$	6.42	tetrahedral
$TiCl_4$	6.58	tetrahedral
$SnCl_4$	6.78	tetrahedral

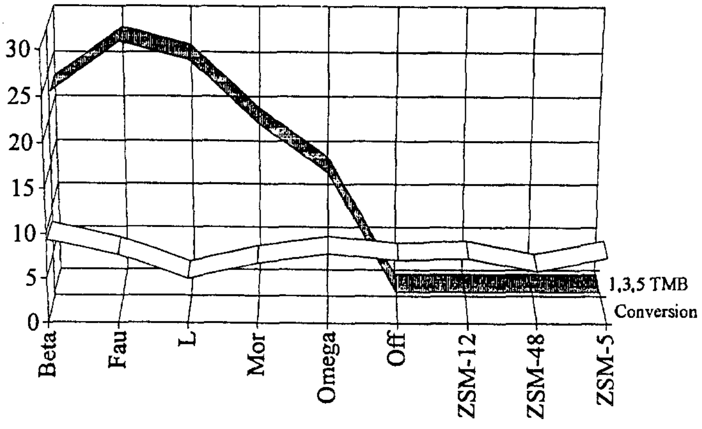

Fig. 5. Conversion of *m*-xylene during its isomerization and amount of 1,3,5-trimethylbenzene obtained over different zeolites; data taken from ref. [16].

choice of the zeolitic structure on the amount of 1,3,5-trimethylbenzene obtained during xylene isomerization [16].

It is clear that, as the pore size of the zeolite structure decreases, the main factor affecting the amount of the large 1,3,5-trimethylbenzene molecule is the space available for its formation and/or diffusion, which explains its steady decrease. As a reference, we should note that conversion is also given to show that these effects are not attributable to conversion level differences.

3.2. SIZE OF THE CRYSTALLITES

As we mentioned before, one of the factors that presents a large importance in the regulation of shape selectivity is the length of the diffusional pathway. Since the effect of shape selectivity is mostly based on the existence of severe diffusional limitations towards some of the species involved, the increase of the diffusional path will always lead to an increase of that effect.

Recently, several results were reported [17,18] both in the field of catalysis and adsorption over zeolites, where a distinct difference in the catalytic or adsorptive behaviour of zeolites is found, according to the size and morphology of their crystallites. As an example we may show some results obtained in the case of an intermediate pore zeolite, ZSM-5, during the alkylation of toluene by methanol over two catalysts with different crystallite sizes, 6 μm and <0.2 μm respectively, but both with the same silicon/aluminium ratio [17]. The comparison is made for identical times-on-stream so that all the changes that are observed in the selectivity can be attributed to the variation of the size of the crystallites.

In fig. 6 the values obtained for the percentage of para isomer, as percent of total

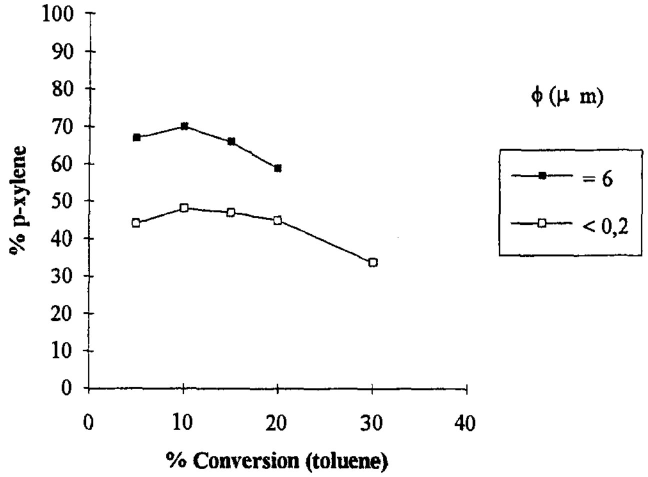

Fig. 6. Percentage of para-xylene obtained on the whole of the xylenes as a function of toluene conversion in the alkylation of toluene with methanol reaction.

xylenes, as a function of the conversion of toluene during the above-mentioned reaction is represented.

The difference found in the xylene distribution is solely due to the decrease of the diffusional pathway, and reaches very significant values (at 10% conversion the increase of the diameter of the crystallites from 0.2 to 6 μm induces an increase in the selectivity towards the para-xylene isomer from 48 to 70%), since the diffusional limitations are directly related to the length of the diffusional pathway.

3.3. CREATION OF EXTERNAL CONSTRAINTS

The deposition of substances over the zeolite's surface presents two important consequences on their selectivity. These effects, as we have said before, are not always easy to discriminate entirely: it decreases the pore size of the catalyst and deactivates a large part of the surface active sites, since it covers them with a different material (see fig. 7) [19].

The chemical vapour deposition technique usually occurs by a surface reaction between the modifying agents and the silanol surface groups [20], as depicted in fig. 8 for the case of tetramethylorthosilicate with the surface of a zeolite [21].

It is this surface compound that produces both of the above-mentioned effects. The deactivation of the surface sites is capable of increasing shape selectivity all by itself, since these active sites have usually a very low selectivity. The decrease of the pore openings increases the molecular sieving effect, leading to an increase of selectivity.

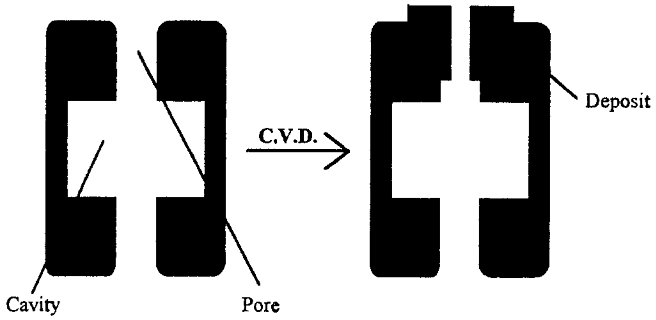

Fig. 7. Schematic representation of the chemical vapour deposition (CVD) technique to decrease the size of the pores of zeolites.

3.3.1. Toluene alkylation by methanol

We present the results obtained with one series of catalysts modified by chemical vapour phase deposition with $SiCl_4$, relative to the effect of decreasing the pore size on the reduction of catalytic activity and the increase of the para selectivity [22].

The silica deposition on the zeolite's surface induces a considerable decrease in the global activity of the catalyst (although comparing at the same conversion level the yield in xylenes is not significantly altered by this treatment). The gain in selectivity towards the para-xylene isomer is, however, considerable as can be seen in fig. 9.

This change can be due to any of the two main effects that are caused by the deposits:

– decrease in the pore openings, with the accompanying decrease of the effective diffusivity of the species inside the porous structure of the zeolite;

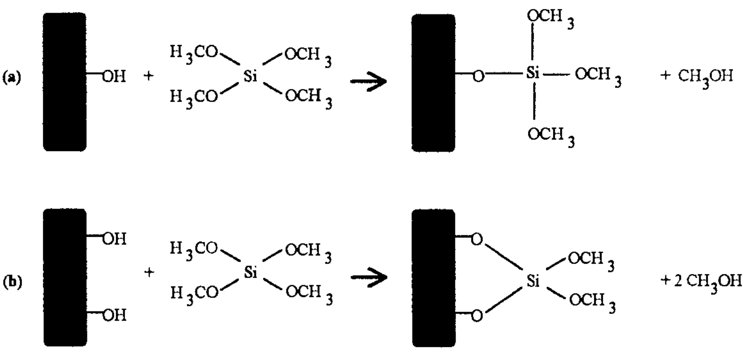

Fig. 8. Representation of the surface reaction between one (a) or two (b) silanol groups with a silicon alkoxide molecule.

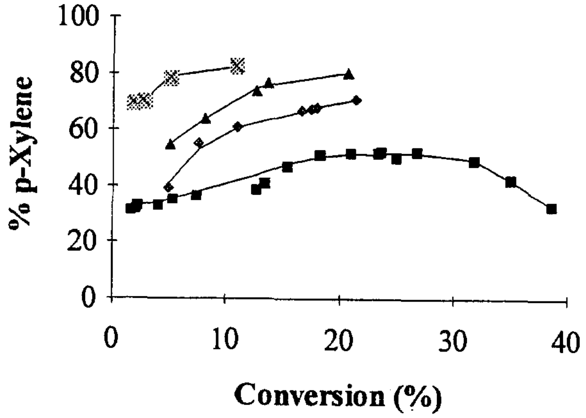

Fig. 9. Percentage of para isomer in the xylenes as a function of conversion, obtained from the alkylation of toluene with methanol over the following catalysts: starting HZSM-5 (■), with 1% (♦), 1.2% (▲) and 3.7% (×) of SiO_2 deposited [22]. Conversion was varied by changing the contact time.

– deactivation of the acid sites that are situated on the external surface of the crystallite; these sites usually present a very low selectivity.

Both factors are conditioning in relation to the global decrease of the activity. This decrease in activity is, in fact, the price one has to pay in order to improve the selectivity.

The larger influence regarding the change in selectivity is probably due to the blocking of the pore openings. This blocking has an effect that will be ever more significant as the amount of silica deposited increases and the isomer, that must diffuse, becomes more bulky, as we have already explained before. The smaller isomer (para-xylene) will be most favoured presenting an increase in selectivity of 42 to 83% (for a conversion level of 10% in toluene and varying only with the amount of material deposited).

These conclusions are still reinforced if we observe the distribution of ethyltoluenes that are produced in this reaction. We see that, as the silica content increases, the selectivity towards the *para* isomers (less bulky than the other ones) also increases, with the concomitant diminishing of the larger isomers (see fig. 10).

We can still look at the influence of the modifying molecule, for instance with catalysts that were treated with $Si(OCH_3)_4$. For a series of catalysts prepared in this fashion we should point out that an XPS surface analysis indicates that the Si/Al ratio goes from 38 in the base catalyst to 100 in a catalyst that was exposed to the above-mentioned modifying molecule for a period of 5 min at 120°C.

For these series of catalysts the results that are obtained for the toluene alkylation by methanol are very conclusive in what concerns the distribution of xylenes. An increase in the selectivity towards the *para* isomers from 73 to 95%, as it is shown in fig. 11.

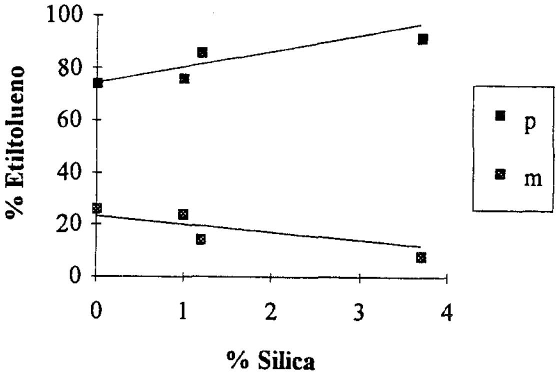

Fig. 10. Distribution of *para*- and *meta*-ethyltoluene isomers as a function of the amount of silica deposited over the zeolite at 10% conversion level [22].

We should point out that the effect induced by this modifying molecule, having a larger diameter than silicon tetrachloride are significantly more pronounced.

3.3.2. Toluene disproportionation and o-xylene isomerization

The same kind of observations can be made in a series of other reactions involving xylenes, as is the case of toluene disproportionation and of *o*-xylene isomerization [19]. Figs. 12 and 13 show results obtained by Murakami, in these two reactions, reinforcing the data previously presented.

The larger the amount of silica deposited on the catalysts surface, the larger the selectivity towards the para isomer will be, and the smaller the overall activity.

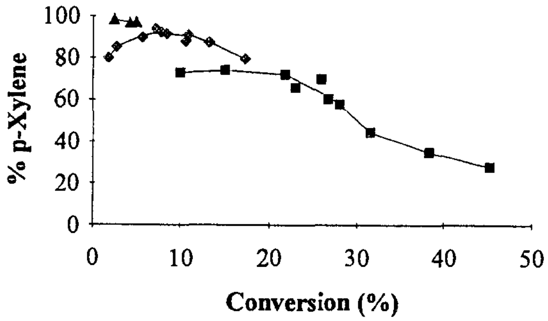

Fig. 11. Relation between the percentage of *para*-xylene, as percent of total xylenes, with toluene conversion in the alkylation of this compound with methanol over catalysts modified with methylorthosilicate; (base HZSM-5 (■), with 5 min treatment (◆), and with 60 min treatment (▲)) [22].

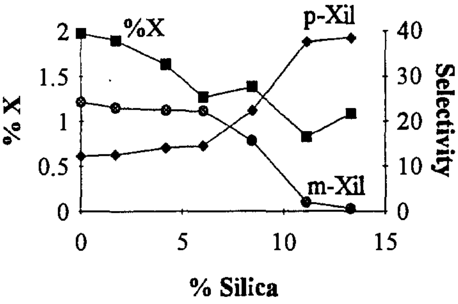

Fig. 12. Data obtained by Murakami et al. for conversion and selectivity as a function of the amount of silica deposited, in the disproportionation of toluene over ZSM-5 [19].

3.3.3. Propene aromatization

Also for ZSM-5 based catalysts, but this time modified with zinc chloride, the results obtained during propene aromatization seem very interesting since a considerable increase in the *para* selectivity is observed as the amount of zinc oxide deposited is increased. These results are shown in table 2 [23].

The increase in the para/ortho ratio in the case of xylenes and ethyltoluenes is to be noted. This effect is also produced by the decrease in the pore aperture, but in the case of zinc a further effect may be considered. The presence of a metal ion on the zeolite surface can make the zinc modified zeolite a bi-functional catalyst, coupling surface metal sites (supplied by the zinc atoms) with the acid sites that are supplied by the zeolitic framework.

3.4. CREATION OF INTERNAL CONSTRAINTS

There are several processes to change the space available in the vicinity of the active sites that are situated inside the porous structure of the zeolites. Apart from

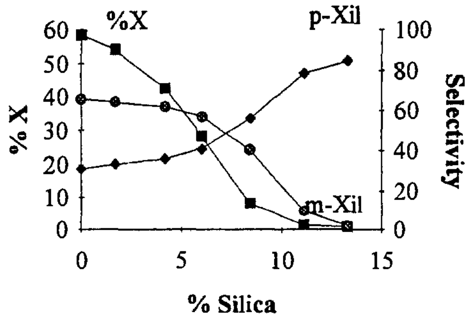

Fig. 13. Data obtained by Murakami et al. for conversion and selectivity as a function of the amount of silica deposited, in the isomerization of *o*-xylene over ZSM-5 [19].

Table 2
Comparison of the distribution of aromatic C_8 obtained in the aromatization of propene over zinc modified ZSM-5 catalysts at 530°C [23]

	HZSM-5	ZnHZSM-5 (1.34%)	ZnHZSM-5 (6.23%)	Thermodynamic equilibrium
p-xylene	59.2	69.6	73.2	23.3
m-xylene	20.2	10.0	9.4	51.0
o-xylene	10.0	4.0	4.0	21.3
ethylbenzenes	10.6	16.3	13.4	4.4
p/*o* xylenes	5.9	17.3	18.1	1.1
p-ET/*m*-ET	2.1	7.4	8.83	–

the methods based on the change of the type and content of the compensating cations [24], as well as those based on the pre-adsorption of polar molecules, such as water or ammonia [25], and which are known for long and lead to changes in the properties of zeolites as molecular sieves for uses in adsorption processes, the deposition of coke or the introduction of other bulky compounds can also influence, to a large extent, the diffusivity of reactive species inside the porous network.

Some of these modifying agents do not induce irreversible changes in the modified material, while others produce permanent structural alterations. Among the latter the following reactive molecules appear to be the most commonly used: silane (SiH_4), disilane (Si_2H_6) and diborane (B_2H_6) [26].

This kind of modification techniques has been mainly used on mordenites [27–29] and the effect of reducing the pore sizes has been analysed mainly for processes involving adsorption and separation of gaseous binary and ternary mixtures [29].

If a correct optimisation and control of the operating conditions are not performed, namely the temperature, there is a large chance of producing modifications of the external surface as well as the reduction of the pore openings [28].

Another commonly used technique in the modification of HZSM-5 zeolites is the impregnation with H_3PO_4 [30–33], which leads to changes both in the activity and in the selectivity, for instance for the selective production of *para*-xylene [32] and the selective synthesis of olefins from methanol. However, little is known about the molecular interaction of phosphoric acid with the zeolite [34], and the uncertainty about the location of the phosphorous compounds is apparent. According to some researchers they are homogeneously distributed inside the zeolite channels [31], while others state that they are concentrated on the external surface of the crystals, close to the pore entrances [30].

4. Final conclusions

Zeolites are appearing, ever more, as catalysts having an enormous potential.

Their large versatility, which is a consequence of the countless structures and composition ranges available, either by direct synthesis or by resorting to a large number of post-synthesis treatments and modifications, allows them to be adapted to a wide variety of chemical processes and reactions. Their current applications and, in particular those resulting from their shape selectivity properties, make them indispensable catalysts in the petrochemical industry. Also the predictable new applications, namely in the area of fine chemicals and organic synthesis, indicate that they will have a bright future in the heterogeneous catalysis field.

Acknowledgement

I am grateful to Professor Michel Guisnet, Dr. N.S. Gnep, Dr. Filipa Ribeiro and Dr. M.H. Vasques for fruitful cooperation and Dr. F. Lemos for critical reading of the manuscript.

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