

IMPROVING THE ACCESSIBILITY AND CATALYTIC ACTIVITY IN ZEOLITES THROUGH THE GENERATION OF HIERARCHICAL POROSITY

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ABSTRACT

A great interest has grown in recent years in the scientific community on the synthesis and application of hierarchical zeolites, i.e. zeolites having at least two levels of porosity. The presence of a secondary mesoporosity, in addition to the typical zeolite micropores, in these materials provides them with singular properties and, therefore, with a high potential for novel applications in different fields.

Hierarchical zeolites possess enhanced textural properties and increased mass transfer rates. As a consequence, they suffer of quite lower steric and diffusion limitations than conventional zeolites, which is especially important properties in the processing of bulky molecules. Hierarchical zeolites have been also reported to show a better resistance to deactivation by coking. In addition, the availability of the additional mesoporosity provides an ideal space for supporting other active phase with a high dispersion and strong interaction with the support, opening new ways for the development of improved bifunctional zeolitic catalysts.

Although selectivity towards the target products may be negatively affected by the occurrence of non-desired reactions over the mesopore surface of hierarchical zeolites, the results so far reported indicate that this does not occur in many cases, hence it is possible to achieve zeolitic catalysts with enhanced accessibility and catalytic activity while preserving at the same time a remarkable selectivity.

Keywords: hierarchical zeolites, mesoporous zeolites.

INTRODUCTION

Zeolites have been traditionally defined as microporous crystalline aluminosilicates, being usually obtained in the form of crystals/particles within the micrometer range. The occurrence of uniform micropores with molecular dimensions (generally 0.4 – 0.75 nm) turns them into molecular sieves. This unique property allows the zeolites to discriminate among different reactants, products or even transition states according to their shape and size and has led to the remarkable selectivities exhibited by zeolites in a large number of reactions.

However, zeolites fail when dealing with bulky substrates, showing low activities, since the latter cannot access the active sites located inside the zeolite micropores. Thus, only those sites situated over the external surface of the zeolite crystals, or close to the micropore openings, are accessible for large molecules. However, these sites represent usually a low share (< 5%) of the total content of active sites. On the other hand, even when the substrate can enter into the zeolite micropores, the diffusion rate is usually too slow, which causes the appearance of intracrystalline mass transfer constraints.

One of the most successful strategies that have been developed in recent years for improving the accessibility in zeolites is likely the case of hierarchical zeolites [1, 2]. These

materials are characterized by the presence of a bimodal pore size distribution, formed by both micropores and mesopores. The secondary mesoporous structure can be generated by a variety of specific synthetic procedures, being responsible for the improved mass transfer properties of these materials, which have proved to be advantageous in numerous reactions. On the other hand, the surface area associated to this secondary porosity implies the presence of active sites that are not sterically hindered for interacting with bulky molecules.

RESULTS AND DISCUSSION

A number of methods have been developed in recent years for the synthesis of hierarchical zeolites. Although all of them lead to materials with bimodal pore size distributions, the features and contribution of the generated secondary mesoporosity depends heavily on the chosen procedure. These synthesis strategies can be classified as follows [3]: a) dealumination, b) desilication, c) hard templating by carbon materials, d) hard templating by polymers, e) incorporation of organosilanes, f) other methods.

The presence of a bimodal micro/mesoporous structure provides hierarchical zeolites with a collection of singular properties [4]: improved surface area, increase in mass transfer rates, better resistance to deactivation and high dispersion of active phases. Figure 1 illustrates how the enhancement of the BET surface area undergone by hierarchical ZSM-5 zeolite depends strongly on the synthesis strategy being applied.

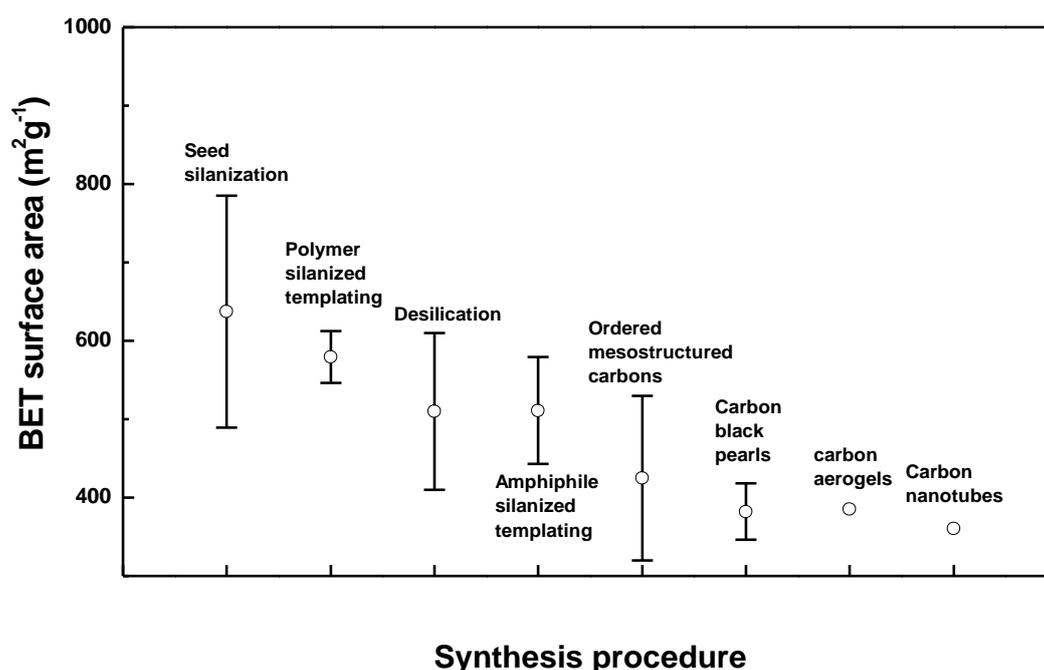


Figure 1. Range of BET surface areas obtained for hierarchical ZSM-5 as a function of the synthesis strategy [3].

For conventional zeolites, having crystal sizes in the micrometer range, the proportion of external surface area is usually negligible, i.e. the BET surface area corresponds almost completely with the surface area associated to the micropores. However, in the case of hierarchical zeolites a great part of the surface area is related to the mesoporosity, while a reduction is usually observed in the micropore surface area compared with conventional zeolites. This is an essential aspect since the mesopore surface area is not sterically hindered,

as it occurs with the surface area of the micropores, being capable of adsorbing and interacting with bulky compounds.

The use of hierarchical zeolites as catalysts in a variety of reactions has demonstrated their large potential and interesting catalytic properties, especially in those reactions wherein steric or diffusion limitations are encountered. Thus, hierarchical zeolites are of high interest in petroleum refining processes since conventional zeolite catalysts cannot refine about 20% of petroleum due to the steric hindrances posed by bulky molecules. The application of hierarchical zeolites may contribute to reduce this proportion increasing meaningfully the profitability of the refining. In addition, it is expected that the yield of gasoline and diesel fractions might also be enhanced by the use of hierarchical zeolite catalysts [5].

Likewise, hierarchical zeolites have been tested in a variety of reactions involving bulky molecules with potential application in the production of fine chemicals, like the protection of benzaldehyde with pentaerythritol, condensation of benzaldehyde with 2-hydroxyacetophenone, the esterification of benzyl alcohol with hexanoic acid and the Friedel-Crafts acylation of aromatic compounds [6, 7]. Superior conversions have been achieved usually over the hierarchical zeolites due to the right combination of improved accessibility provided by the mesopores and its strong acidity and high crystallinity.

Hierarchical zeolites have been also investigated in a number of reactions within the field of environmental catalysis. Likewise, hierarchical zeolites have shown to be remarkable catalysts for the cracking and conversion of plastic wastes. These residues are formed by bulky substrates wherein an easy access to the acid sites leads towards higher activities. The improved accessibility present in hierarchical zeolites for bulky polyolefin molecules caused a strong increase in the polymer conversion compared to conventional and nanocrystalline zeolites [8], as it can be observed in Figure 2.

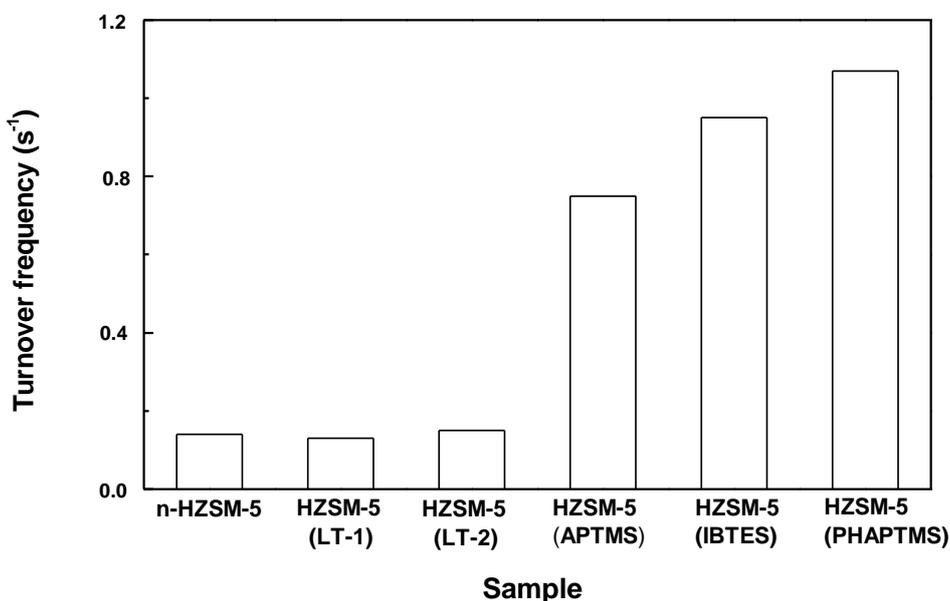


Figure 2. Activity obtained in the conversion of waste polyethylene at 360 °C, over hierarchical (three right samples) and nanocrystalline (three left samples) HZSM-5 materials.

Also within this field, the decomposition of NO over hierarchical Cu-ZSM-11 and Cu-ZSM-5 is another reaction that deserves special mention [9]. In this case, the improved

accessibility causes an enhanced activity of the hierarchical zeolites because of the formation of dimeric and oligomeric Cu species within the mesopores instead of the preferential formation of monomeric Cu species over conventional Cu-ZSM-11 and Cu-ZSM-5.

CONCLUSIONS

The development of hierarchical zeolites is changing the conventional vision of zeolites as just purely microporous materials with shape selectivity properties. At present, the occurrence of mesoporosity is becoming in many cases an added and valuable feature for zeolites as it causes the improvement of their properties: enhanced textural properties, faster intraparticle transport, reduction of steric and diffusion constraints, improved dispersion of active phases and better resistance to deactivation. As a result, hierarchical zeolites typically show a higher catalytic performance compared to conventional ones in a large variety of reactions, which does not imply necessarily a decrease in the selectivity exhibited by these materials.

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