Benefits of hierarchization of HMFI zeolites on the coke management

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Introduction
Many zeolite catalysts currently used commercially are already hierarchical: FCC, hydroisomerization and hydrocracking being the most important examples in oil refining. In these cases, hierarchization is brought by steam and/or acid treatments where Al is selectively removed from the framework. Recently, other methods have been rediscovered (caustic treatment where Si is removed to a greater extent than Al), studied in-depth by modern techniques and new methodologies created (fluoride treatment where Si and Al are removed at and equal rate). Moreover, the production of nanosized zeolite crystals is equivalent to hierarchization as a sizable (mesoporous) surface is developed on their external surface. This contribution focuses on the effect of hierarchization on cracking and regeneration of ZSM-5 zeolite catalysts in hydrocarbon methylcyclohexane (MCH) and ethanol (EtOH) transformations. Two parent ZSM-5, one made of micron-sized crystals and the other containing nano-sized crystals were studied as well as their off springs produced by caustic and fluoride treatments.

Materials and Methods
The starting material, NH4-ZSM-5 (Si/Al=19), is a commercial micro-sized zeolite provided by Clariant. Two hierarchical ZSM-5 zeolites, A and B, were derived from P using acidic and basic post-synthesis treatments, respectively. For sample A, the fluoride treatment was performed as described by Qin et al.[1] For sample B, the alkaline treatment was performed as described by J.C Groen et al.[2]. A nano-sized commercial zeolite NH4-ZSM-5 (noted N) with Si/Al = 41, from Clarian, was also used in this work.

Results and Discussion
The effects of two different hierarchization procedures (alkaline and fluoride leaching) on the performances of ZSM-5 catalysts in the transformation of methylcyclohexane at 723K are highlighted and discussed in relation to their porosities. The hierarchical catalysts exhibit different porosities; namely, the fluoride treatment leads to a zeolite combining micropores and macropores while alkaline leaching adds mesopores interconnected with the native micropores.

While the initial activities and selectivities of catalysts derived from the P, A, B zeolites are very similar in the conversion of methylcyclohexane, the presence of mesopores (alkaline leaching), close to the active sites, greatly improves the stability of such a hierarchical catalyst by favoring the desorption of products. This behavior is similar to a reduction in zeolite crystal size. This increased stability is not due to a decrease of the coke toxicity, but rather to an inhibition of the growth of coke precursors, in turn related to the shorter diffusion paths of reactants and products. Two types of coke are present on the meso-micro-porous zeolite: (i) a “light coke” composed of alkylbenzenes strongly adsorbed on Lewis acid sites and silanols, (ii) a “heavy coke” (alkylphenanthrenes and alkylpyrenes) trapped at the intersection of the zeolite channels. While the light coke has no impact on the catalyst stability, the heavy coke poisons active sites, most probably remote from the mesopores.

During the ethanol-to-hydrocarbons (ETH) transformation at 623K and 3.0 M Pa on HZSM-5 zeolites, unwanted side reactions occur and lead also to the formation of coke. Its composition is strongly related to the dimensions and shape of the ZSM-5 pores; the structures of molecules trapped are similar than these found in MCH. The coke rate depends on the textural properties of materials and more particularly on the diffusion path length. But the catalyst lifetime is not correlated to the coking rate, it is related to the external surface, since the ethanol transformation occurs mostly by pore mouth catalysis. Additions of macropores (A) by fluorine leaching or mesopores by alkaline treatment (B) of micron-sized zeolite (P) are simple tools to increase the number of pore mouths. But, by far, the most efficient way to increase dramatically the number of pore mouth is to reduce their crystal size. The highest catalyst longevity (>100 h), is obtained in spite of a total poisoning of acid sites on hierarchical nanometer-sized zeolite (N).

The decrease in the diffusion path also offers a clear advantage in the catalysts regeneration by lowering the temperature of total coke removal.

Conclusion
The time on stream behavior of the various catalysts shows the advantages of hierarchization and particle size. The deactivated catalysts are extensively characterized by their residual acidity and pore volumes, nature and quantity of the carbonaceous residues and ease of decoking. One important feature is that nanosized and hierarchical zeolite crystals produce less of the very toxic coke molecules (located at channel intersections) because most coke precursors diffuse efficiently to the external surface where their deleterious effect is minimal. Nanosized ZSM-5 are systematically better than any hierarchical zeolites produced by post-synthesis treatment due, among other factors, to the much lower diffusion pathways molecules have to follow in the microporous channels.

Significance
Like any other reactions, coking and coke removal by combustion can be optimized by an a priori rational design of the zeolite properties using new preparation methodologies supported by advanced characterization of zeolite based catalysts.

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