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Catalysis with hierarchical zeolites

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ABSTRACT

Hierarchical (or mesoporous) zeolites have attracted significant attention during the first decade of the 21st century, and so far this interest continues to increase. There have already been several reviews giving detailed accounts of the developments emphasizing different aspects of this research topic. Until now, the main reason for developing hierarchical zeolites has been to achieve heterogeneous catalysts with improved performance but this particular facet has not yet been reviewed in detail. Thus, the present paper summaries and categorizes the catalytic studies utilizing hierarchical zeolites that have been reported hitherto. Prototypical examples from some of the different categories of catalytic reactions that have been studied using hierarchical zeolite catalysts are highlighted. This clearly illustrates the different ways that improved performance can be achieved with this family of zeolite catalysts. Finally, future opportunities for hierarchical zeolite catalysts are discussed, and the virtues of various preparation methods are outlined, including a discussion of possible pitfalls in the evaluation of new, potential hierarchical zeolite catalysts.

1. Introduction

During the last decade, the scientific literature on hierachical zeolites has dramatically increased, and several reviews highlighting various aspects of the recent developments have already appeared [1–7]. The term hierarchical zeolites refers to zeolites featuring at least one additional level of porosity besides the intrinsic micropore system characteristic of zeolites. In practice the term most often refers to mesoporous zeolites, i.e. hierarchical zeolites featuring additional porosity in the mesopore size region (pore diameters in the range 2–50 nm) because the major impact of auxiliary porosity on catalysis stems from porosity in this size region. Interestingly, it is difficult to trace the true origin of hierarchical zeolites, and their use as heterogeneous catalysts, since it is more or less hidden in the patent literature. However, with the current knowledge about these materials and their preparation methods there is no doubt that several early patents describe methods for preparing such zeolite materials, and also their use as heterogeneous catalysts in various reactions [8–11]. One reason that it is often not trivial to conclude when hierarchical zeolites were claimed in the patent literature is that the physical-chemical characterization reported originally does not provide direct evidence for the detailed structure of the materials studied. Thus, much of the recent interest in hierarchical zeolites can be ascribed to improved methods for visualization of the structure of these materials, and particularly to the wider availability of sufficiently elaborate electron microscopy techniques, such as high-resolution TEM and TEM tomography. With these methods, the structure of hierarchical zeolite catalysts can de deduced in impressive detail, and the observed catalytic performance can more easily be related to their structure. However, it is still necessary also to use various other physical–chemical characterization methods to establish that the structural modification of hierarchical zeolites has not lead to significant changes in other catalytically important properties of the zeolite, especially with respect to zeolite acidity. Only this way, reliable structure-activity relationships can be quantitatively established.

Here we present a review of the literature reporting the use of hierarchical zeolites as catalysts for different reaction types. The reactions types are divided into classes comprising alkylation, methanol-to-hydrocarbons (MTH) and olefin aromatization, isomerisation, cracking, condensation and other, more specific, reactions. The alkylation, isomerisation and cracking reactions share the same carbenium chemistry and could be viewed together. However, since the size of the substrates used and the operating temperature differs widely in these three categories, the effect of mesopores also differs and they are therefore treated separately.

One of the major limitations for the use of zeolites as catalysts is the limited access to the active sites within the individual crystals. This attribute serves as the material's strength (allowing for shape selectivity) as well as a weakness (mass transport limitations). It is predicted that mesoporous zeolites can contribute

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Table 1
Overview of the different reaction classes and the main effect of mesoporous zeolites.

Reaction type	Main observation
Alkylation reactions	Higher activity
Transalkylation reactions	Improved stability
Isomerisation reactions	Higher activity
Cracking of light substrates	No significant improvement
Cracking of heavy substrates	Substantially higher activity
MTH and aromatization reactions	Longer catalyst lifetime
Condensation reactions	Higher activity. Higher selectivity towards bulky products

to the field of catalysis in either of two ways. These hierarchical materials can potentially increase the number of reactions in which zeolites are used by allowing acceptable mass transport of larger reactants and products and allowing for reactions catalyzed by strong acidity to proceed on the mesopore surface and pore mouth. Alternatively mesoporous zeolites can simply serve by improving existing reactions/processes currently using zeolite catalysts. It is here illustrated how examples of both applications exist in literature. A summary of the major trends observed for hierarchical zeolites categorized by reaction type is shown in Table 1.

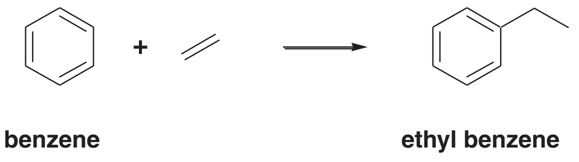
2. Alkylation reactions

Alkylations and acylations are important reactions in industry for which zeolites find use. Unfortunately, these processes are rarely operated at full potential due to mass transfer limitations within the zeolite catalysts; therefore, the advantages of applying mesoporous zeolites as catalysts for these transformations are obvious. In the literature, several reports are available dealing with mesoporous zeolites for such transformations, particular with alkylation of benzene. The general finding in these reports is the observation that mesoporous zeolites are more active for these transformations. This is expected due to shorter diffusion path length in mesoporous zeolites, however, what is perhaps not so obvious is why also an increased selectivity to monoalkylated products is observed.

2.1. Benzene alkylation

Christensen et al. [12] reported the use of mesoporous ZSM-5 prepared by carbon-templating for gas phase alkylation of benzene with ethylene (Scheme 1).

The authors used a molecular ratio of benzene:ethylene of 5.1:1, pressures from 2.5 to 5 bar and temperatures from 583 to 643 K. Undesired side reactions include the formation of di- and tri alkylated ethyl benzenes as well as numerous alkylated benzenes arising from transalkylation of the product. It was shown, that the mesoporous zeolite was significantly more active than the conventional zeolite catalyst. Moreover, it was shown that the selectivity towards ethyl benzene was significantly higher using the mesoporous zeolite and that the effect was even more pronounced at high conversions. The increased selectivtity towards the monoalkylated product, ethyl benzene, can be understood by looking at the schematic representation in Fig. 1 of the relative concentration profiles of benzene, ethylene and ethyl benzene [13].



Scheme 1.

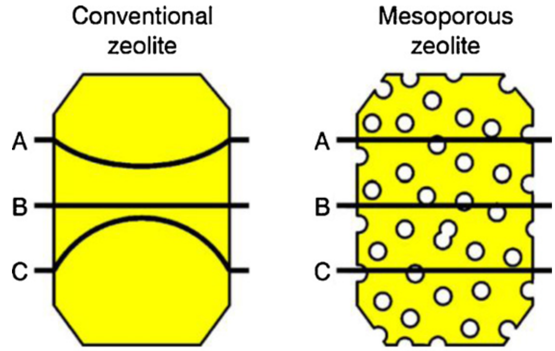


Fig. 1. Schematic of the relative concentration profiles (disregarding molecular adsorption) of benzene (A), ethylene (B) and ethyl benzene (C) in conventional and mesoporous ZSM-5 during alkylation of benzene with ethylene (figure reproduced from Ref. [13]).

The concentration profiles illustrated in Fig. 1 were derived from a classical evaluation of diffusion properties of the benzene, ethylene and ethylbenzene under actual operating conditions, showing that benzene and ethylbenzene are diffusion limited if the crystals are too large [13]. The concentrations of reactants and products in the zeolite and in the gas phase are likely different due to adsorption. However, as benzene is consumed in the alkylation reaction, a concentration gradient enriched in ethylbenzene and depleted in benzene is expected to be present in the conventional sample where diffusion restraints are pronounced. It is clear that if a relatively higher concentration of ethylbenzene exists in the interior of the crystal, this must lead to the formation higher levels of diethylbenzene. In other words, diffusion limitations in conventional crystals during alkylation of benzene with ethylene lead to higher levels of polyalkylated products than desired. On the contrary, in case of the mesoporous crystal, having a shorter average diffusion path length, the concentrations of ethylbenzene and benzene throughout the crystal will be much closer to the value strictly determined by gas phase concentration and adsorption affinity. In effect, successive alkylation of ethylbenzene is not as likely to occur in the mesoporous zeolite as in the case of the conventional one, and the monoalkylated product is predominant.

Dealumination of mordenite has been well understood for several decades but recently also base treatment (desilication) of mordenite, either alone or in combination with dealumination, has been successfully performed to obtain similar advantages.

In close relation to the previous example Groen et al. [14] compared a mesoporous mordenite catalyst obtained by desilication to a commercial sample with a smaller crystal size and higher acid density in the liquid phase benzene alkylation with ethylene. Despite the advantage with respect to crystal size and acidity, the hierarchical mordenite showed an initial higher activity in comparison with the commercial mordenite. Much more pronounced though was a remarkably slow deactivation of the mesoporous sample coupled with a slightly higher selectivity towards the desired ethyl benzene. The improved catalytic performance as discussed above was attributed to the enhanced mass transport. This report is a particularly interesting case where the authors chose to use the zeolite in the liquid phase where mass transport limitations pose much greater problems as compared to gas phase reactions. Nevertheless liquid phase reactions represent an interesting area in which mesoporous zeolites can find applications.

Three different commercially available mordenite samples were desilicated and tested in liquid phase benzene alkylation with propene producing cumene (iospropylbenzene) in a study by de Jong and co-workers [15]. The mordenite samples were outside the optimal window with respect to Si/Al ratio for desilication [16] but with an increased concentration of sodium hydroxide mesopore