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Manipulating the architecture of zeolite catalysts for enhanced mass transfer

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Zeolites belong to microporous solids that are widely used as adsorbents, catalysts and catalyst supports. As diffusion in the microspores is slow, it is highly desirable to develop approaches to enhance mass transfer or to avoid the negative effect from mass transfer resistance. In this perspective, we underline pore architecture control for hierarchical zeolite, and spatial locations of metal nanoparticles on zeolite. For solid acid catalysts, the construction of auxiliary porosity in crystalline zeolites leading to the formation of hierarchical zeolite is a promising solution. Most successful pore-architecture construction strategies are based on templating approaches within the classic LaMer crystallization framework, whereas our strategies are based on the non-classic orientated attachment growth mechanism in dry gel crystallization. Organic additives, such as organosilanes, can be incorporated with protozeolite particles to produce hybrid mesocrystals. Combustion of organics in the mesocrystal affords hierarchical beta zeolites, the pore-architecture of which is tunable with respect to additive selection. Such a crystallization based design of pore-architecture merits small primary crystal size and improved pore-connectivity, which have been verified to be the key factors that affect diffusion. On the other hand, for zeolite supported metal catalysts that suffer from deactivation caused by pore blocking, we propose a strategy to avoid the deactivation problem by depositing metal nanoparticles exclusively on the external surfaces of support. This can be achieved by simply leaving the structure directing agents in the pores before supporting metal particles. Side reactions caused by diffusion resistance are minimized, and moreover, the involatile byproducts, if any, do not produce additional diffusion resistance. Such a simple yet effective architecture control significantly prolongs the lifetime of Au/TS-1 catalyst in direct propene epoxidation with H_2 and O_2. From these demonstrations, it is important to design purpose-orientated zeolite synthesis to enhance mass transfer, for which the architecture plays a key role.

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Introduction

Zeolites are three dimensional crystalline porous solids possessing pore channels normally less than 2.0 nm, which lay in the microporous range according to the IUPAC classifications. They are widely used as catalysts, catalyst supports, adsorbents for gas separation/purification, or ion-exchangers in laundry powders or treatment of toxics. On one hand, the successful use of zeolites is largely attributed to their crystalline framework structures that endow them high (hydro) thermal stability, strong acidities, tunable Si/Al ratios, and easy isomorphous substitution by other metals (B^{3+}, Fe^{3+}, Ga^{3+}, Ti^{4+}, Ge^{4+}, among others). Their precise pore apertures and cavity structure make them unique shape-selective catalysts and adsorbents. Henceforth, they are also referred to as molecule sieves. On the other hand, artificial zeolites that are mass produced nowadays at industrial scale are comprised of micron-sized crystals, and the solely presence of micropores brings about mass transfer problems that is associated with slow diffusion in micropores. Moreover, bulky molecules whose sizes exceed the size of micropores are denied access to the micropores and thus the catalytic reactions only take place on the external surface. These drawbacks have limited the applications of zeolites toward treatment of large molecules and also called upon research effort to alleviate such problems. Several synthetic strategies for nanozeolites [1•], hierarchically porous zeolites (HPZs) [2–6], extra-large pore zeolite [7], or 2D structured zeolites (through top-down delamination [8–10], bifunctional structural directing agent [11,12], or crystallization control [13]) have been reported so far. Recently, desilication and recrystallization methods to generate HPZs have appeared in commercially viable pilot scale demonstrations [14•,15•]. From the industrial viewpoint, the appealing fabrication methods should be simple and easy for scaling-up, and use low-cost starting materials.

In addition to direct use as solid acid catalysts, zeolites are also applicable as metal supports for bifunctional catalysts. In this case, the spatial distribution of metal centers can affect the mass transfer and accessibility as well. Consequently, the position of metal centers can have substantial influences over catalytic performances. To achieve reactant shape selectivity, it is desirable to synthesize metal@zeolites structure whereby metallic particles core are fully encapsulated by zeolite shells, as recently exemplified by Goel *et al.* [16••] and Bao *et al.* [17]. For reactions that metal-support synergy is important but no shape-selectivity is required, it is important to enhance the mass transfer by placing metallic particle at the external surfaces of zeolitic crystals.

In view that the importance of pore-networks for hierarchically nano-porous and macro-porous systems have been rationalized by Rao and Coppens [18,19], herein we underline the importance at the micro-porous and meso-porous scale to catalytic performance. In this perspective article, we intend to give a brief review on the preparation protocols of HPZs that have been achieved recently, with anemphasis on 'pore-architecture' engineering through non-classic orientated attachment (OA) crystallization. We also give some successful examples on zeolites supported metal catalysts design, where 'spatial-distribution' engineering will be underlined. By both types of catalysts design, we manifest that the 'architecture', alternative to composition, is an important way to enhance mass transfer or to reduce mass transfer effect, and can have beneficial consequences on the performance of the catalytic processes.

Hierarchically porous zeolites: pore-architecture engineering

The mass transfer and reaction kinetic interplay has been recognized in reaction engineering for a long time and the theoretical basis to understand the effect of mass transfer was established by E.W. Thiele: The Thiele modulus dictating the utility of zeolite catalysts. As the diffusion for a given molecule in a particular micropore channel is fixed, the enhancement of mass transfer for nanozeolites or HPZs stems from a shortened diffusion path [20]. Besides, for HPZs, more and more evidences clearly manifest that it is not the presence of auxiliary pores that is important, it is crucial whether the pores are connected to the external surface or not [21••,22•,23,24••]. Weitkamp *et al.* [23] have demonstrated through Pulse Field Gradient (PFG) NMR technique that the intracrystalline mesopores in USY zeolites has negligible effect for mass transfer of *n*-octane and 1,3,5-triisopropylbenzene with respective to conventional Y zeolites. Pérez-Ramírez *et al.* [21••,24••] have reported the use of positron annihilation lifetime spectroscopy (PALS) to measure pore connectivity and correlate it with catalytic behavior. It has been found that the connectivity determines the 'quality' of mesopores, and the conclusion is in line with other experimental observations [14•,22•]. The above considerations highlight the importance of zeolite crystal size and pore-connectivity to the enhancement of mass transfer, as both factors determine to which extent improvement can be made.

Retrospectively, the first HPZ ZSM-5 with convincing evidence for two sets of porosity has been reported by Jacobsen *et al.* [4] using carbon black Black Pearls 2000 as hard templates. Afterwards, several soft templating routes using functionalized silanes, cationic polymers or amphilic silanes have been mapped out to generate HPZs [25–28]. Meanwhile, Pérez-Ramírez *et al.* [29] have reported the low-cost postsynthetic desilication method to generate several HPZs, and the pore-connectivity as well as the catalytic merits have been demonstrated recently [2,24••]. The top-down methods using layered zeolitic prephase have also been developed over the years, and the method is applicable to a series of framework structures [10]. More recently, a series of designed bifunctional structure directing agents (SDAs) have been found to be able to tailor the thickness of zeolite layers down to unit cell scale by Ryoo *et al.* [12], and the HPZs obtained have demonstrated superior performance in heterogeneous catalysis, for instance, the prolonged lifetime in reactions. Tsapatsis *et al.* [13] demonstrated another possibility to control the morphology of intergrowth of MFI and MEL structure by a co-templating strategy, where the branching of growth is tailorable to afford a house-of-cards structure. A method to create mesoporous zeolite composites without the need for separate SDA to generate the mesopores has already introduced by Wang and Coppens in a series of articles [21••,22•,23,24••,25–32]. As more extensive reviews have appeared [3,5,8,33], we will not elaborate the topic of HPZ synthesis.

Recently, a series of synthetic protocols have been developed in our lab to generate HPZs with diverse topologies [34••,35–38]. An interesting finding from the monitoring of zeolite beta crystallization in a dry gel conversion (DGC) system is that it observes the non-classic OA crystallization pathway. The starting gel undergoes morphology changes during steam assisted crystallization (SAC) treatment, and evolves into discrete tiny particulates of 20–30 nm in 6 h. These particulates aggregate in to nanozeolite assemblage of 90–200 nm in ca. 16 h. Bulky zeolite crystals of >200 nm are finally formed as a result of further alignment. The concurrent X-ray diffraction (XRD), Infrared (IR), Scanning electronic micrographic (SEM) and transmission electronic micrographic (TEM) measurements indicate that a temporal overlap of order development has occurred. The whole process is sketched in Route 1 of Figure 1. Evidently, the crystallization can be attributed to the OA growth mechanism and the tiny particulates can be regarded as building blocks, which are transformed into big crystals after disappearing of grain boundaries. The same phenomenon has also been observed by Matsukata *et al.* [39•] and Bein *et al.* [40•], but the formation mechanism has not been further explored, partly because the OA growth mechanism has not been widely accepted in zeolite community. The OA growth mechanism allows us to design new routes to fabricate HPZs, by interrupting the growth process after the formation of protozeolite particulates and still before their further growth by aggregation. Two types of organosilanes have been utilized for this purpose. When hexadecyltrimethoxysilane has been introduced into the precrystallized dry gel by simple impregnation in ethanol solution and drying in the open, a resumed crystallization has afforded a hierarchical beta with mesopore size between 20 and 60 nm (Route 2 of Figure 1) [34••]. Hexadecyltrimethoxysilane resembles surfactants