REDUCING DIFFUSION LIMITATIONS THROUGH RATIONAL DESIGN OF HIERARCHICALLY STRUCTURED CATALYSTS - APPLICATION TO THE ALKYLATION OF BENZENE WITH ETHYLENE

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Abstract

Industrial catalysts often operate in the diffusion limited regime, which reduces overall yields. By structuring the pore network in an optimal, hierarchical fashion, such diffusion limitations can be reduced significantly, resulting in increased yields when compared to conventional nanoporous catalysts. Despite considerable progress in hierarchical synthesis methods and computation, much work remains empirical, and progress on both fronts is rarely merged to enable rational design of the catalyst structure on multiple length scales. We discuss the rational design of hierarchically structured zeolite catalysts, using model driven optimization of the pore network. The alkylation of benzene by ethylene to produce ethylbenzene is chosen as a case study. To test the capability of the mathematical model to qualitatively predict the performance of hierarchically structured zeolites, experiments with meso/macroporous zeolite composites characterized by varying pore network properties and fraction of zeolite crystals are carried out in an isothermal fixed bed reactor. Our results show that model based optimization of the broad pore network can be used to guide the synthesis of porous catalysts with superior overall properties, rather than just optimization at the active-site level.

Keywords

Diffusion limitations, hierarchically structured zeolites, pore network optimization.

Introduction

Diffusion limitations strongly impact the activity and selectivity of industrial micro- and mesoporous (nanoporous) catalysts. By structuring the pore network in an optimal fashion, it is theoretically possible to increase the productivity of the catalyst as well as the stability to deactivation (Rao and Coppens, 2012). Simultaneously, over the past decade or two, there has been an explosion in material synthesis techniques, allowing for the control of pore scale architecture at multiple length scales (Wang et al., 2007). However, the issue of transport limitations at the scale of the catalyst pellet is often neglected and, thus, the carefully tailored properties at the nanoscale are often not retained at the level of the pellet or the reactor. It is therefore of significant industrial interest to optimize the pore network of hierarchically structured catalysts and use the results to guide the synthesis of improved catalysts.

As a first step in this direction, the pore network of a hierarchically structured zeolite catalyst containing a zeolite phase and a meso-macroporous phase is numerically optimized by varying the volume fraction of the zeolite in the composite. The mesoporous phase has a fixed pore volume and diameter. Therefore, varying the zeolite content also changes the mesopore network properties on a total volume (zeolite plus mesoporous

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phase) basis. All calculations are performed using the software package Athena Visual Studio. The performance of the different zeolite composites is evaluated by comparing the volume integrated reaction rate over a single catalyst pellet as a function of the total meso- plus macroporosity. In the next step, hierarchically structured zeolite composites are synthesized by physically mixing together zeolite crystals with an amorphous, mesoporous silica phase. These composites are then pelletized, which introduces macroporosity and then used in fixed bed reactor experiments to determine whether the conversion of the limiting reactant is influenced by the pore network properties of the composites.

Results and Discussion

The alkylation of benzene by ethylene over H-ZSM-5 to produce ethylbenzene was chosen to demonstrate this approach. This reaction is strongly diffusion limited and, hence, optimization of the pore network may enable a higher conversion to ethylbenzene. A mathematical model of a single catalyst pellet was constructed by modeling diffusion through the meso- and macropores using the random pore model of Wakao and Smith (1962), and assuming reaction in only the zeolite crystals. Diffusion and reaction within the zeolite crystals was modeled separately by combining quantum chemical calculations with the ideal adsorbed solution theory and the Maxwell-Stefan equations for intracrystalline diffusion (Hansen et al., 2009), to calculate a local effectiveness factor. The volume integrated productivity is given by:

$$\text{Productivity} = \int_{V_P} \varepsilon_z \rho_z r(p_1, p_2..)\, dV \qquad (1)$$

In Eq. (1), V_P is the volume of the catalyst pellet, ε_z is the volume fraction of zeolite in the pellet, ρ_z is the density of the zeolite, r is the effective rate of reaction in a zeolite crystal (accounting for possible diffusion limitations within) and p_i is the partial pressure of species i.
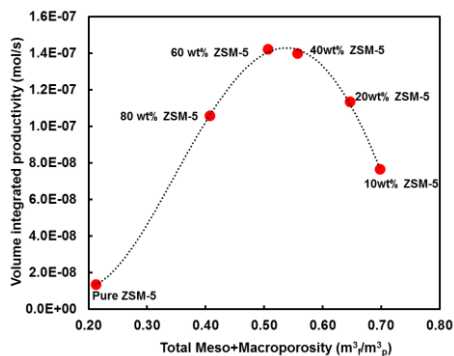

Figure 1. Simulation results for the volume integrated productivity of a single catalyst pellet as a function of the total meso+macroporosity. Pellet diameter = 1.6 mm, Total pressure = 5 bar, Temperature = 653K.
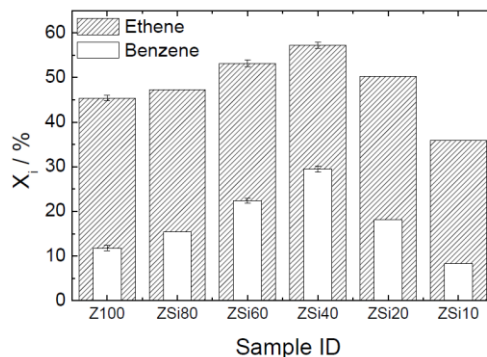

Figure 2. Conversion of ethylene (limiting reactant) and benzene for different macro/mesoporous zeolite composites (the number denotes the weight percentage of zeolite in the composite) in isothermal fixed bed experiments. Pellet diameter = 280 μm. Total pressure = 1 bar, Temperature = 623 K.

Both single pellet simulations and experiments with the various mesopore-zeolite composites showed the presence of a clear maximum indicating an optimal trade-off between the amount of active phase (for reaction) and meso/macropore space (for diffusion). The hierarchically structured zeolite composites yield a much higher productivity compared to the pure ZSM-5 catalyst, indicating that macroporosity at the pellet scale alone is not sufficient to overcome diffusion limitations. Finally, the qualitative trends between modelling results and experiments are in agreement, providing strong support for the use of model based pore network optimization to guide the synthesis of catalysts with high overall performance.

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