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Surface barriers as dominant mechanism to transport limitations in hierarchically structured catalysts – Application to the zeolite-catalyzed alkylation of benzene with ethylene

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HIGHLIGHTS

- The total meso- plus macroporosity of a hierarchical zeolite must be optimized.
- The reaction yield for benzene ethylation is doubled over a pure zeolite pellet.
- Modeling results are compared with fixed bed reactor experiments.
- Surface barriers might limit the performance of hierarchically structured zeolites.

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ABSTRACT

The meso-macropore network of a hierarchically structured zeolite catalyst is numerically optimized to maximize the volume-integrated reaction yield in the ethylation of benzene to produce ethylbenzene over zeolite H-ZSM-5. A hierarchical approach is used at multiple length scales to determine the optimal pore network properties. The maximum volume-integrated reaction yield of the hierarchically structured zeolite catalyst containing meso- and macropores is nearly twice the yield of a zeolite pellet containing only macropores, at the same macroporosity. To bridge the gap between modeling and experiments, a series of physical mixtures of ZSM-5 crystals and mesoporous silica, containing different weight fractions of zeolite is synthesized and used in fixed bed reactor experiments to determine the optimal pellet structure to maximize the conversion of ethylene. Comparison with reactor simulations of the zeolite composites shows that the performance of the zeolite composites might be limited by surface barriers at the external surface of the zeolite crystals, rather than by diffusion limitations within the meso-macropore network of the pellets.

1. Introduction

Rational catalyst design often focuses on the nanoscale, where it is aided by insights from both quantum chemical calculations [1] and experimental characterization methods, such as spectroscopy and electron microscopy [2,3], approaching atomic resolution, to identify the nature of the active surface species, elucidate the role of active sites in reaction mechanisms and inform intrinsic kinetics. Over the past twenty years, there has also been significant development in the availability of material synthesis techniques, which allow for increasing control over the pore structure of a catalyst at multiple length scales [4–6]. However, this microscopic design framework tends to neglect the equally important task of preserving the tailored properties of a catalyst up to macroscopic length scales, namely those of the catalyst pellet and the reactor it is used in. The latter is relevant in practical applications [7–13], where catalyst performance is often limited by diffusion limitations and catalyst deactivation. Therefore, the topic of rational catalyst design must encompass all length scales. It is crucial to identify those features of the pore network in a catalyst pellet that significantly influence catalyst performance for industrially important reactions, such as reforming and alkylation. Doing so will enable the catalyst manufacturer and the process licensor to reduce the time

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List of symbols

$[B]$	matrix of Maxwell Stefan mobilities and loadings
$Đ_i$	corrected diffusivity or mobility of species i in the zeolite (m^2/s)
$D_{e,i}$	effective diffusivity of species i in the mesopores ($m_f^3/m_g/s$)
$D_{E,i}$	effective diffusivity of species i in the macropores ($m_f^3/m_p/s$)
D_{ij}	binary diffusivity of species i and j ($m_f^3/m_f/s$)
D_{Ki}	Knudsen diffusivity of species i ($m_f^3/m_f/s$)
F_i	molar flowrate of species i (mol/s)
F_t	total molar flowrate (mol/s)
k_f	forward rate constant for the benzene alkylation reaction, (1/s)
k_b	reverse rate constant for the benzene alkylation reaction, (1/s)
L	length of the catalyst bed (m_r)
N_i	flux of species i ($mol/m^2/s$)
p_{is}	partial pressure of species i (Pa)
p_{is}^s	partial pressure of species i at the external surface of the zeolite, grain or pellet (Pa)
p_t	total pressure (Pa) or (bar)
q_{is}	molar loading of species in the zeolite (mol/kgcat)
q_{is}^s	molar loading of species at the external surface of the zeolite (mol/kgcat)
r	rate of reaction (mol/kgcat/s)
R	radius (m)
R_g	universal gas constant (J/mol/K)
T_s	temperature (K)
x	conversion
z	axial coordinate along the length of the fixed bed reactor (m_r)

Greek

α	surface permeability (m/s)
$[\Gamma]$	matrix of thermodynamic correction factors
ε	porosity, (m_f^3/m_g^3 or (m_f^3/m_p^3)
ε_z	volume fraction of zeolite within the grain (m_{cat}^3/m_g^3)
η	effectiveness factor
λ	number of Brønsted acid sites per unit cell
v_i	stoichiometric coefficient of species i
ξ	radial coordinate (m)
ρ	density (kg/m^3)
τ	tortuosity factor

Subscripts

0	reference or initial value
Bs	benzene within the porous catalyst
Es	ethylene within the porous catalysts
EBs	ethylbenzene within the porous catalyst
$E+B,H^+$	Co – adsorbed ethylene plus benzene on the Brønsted acid site
EB,H^+	adsorbed ethylbenzene on the Brønsted acid site
g,$grain$	grain level
m	mesopores
M	macropores
p,$pellet$	pellet level
s	porous catalyst
Si	mesoporous silica
z	zeolite

and effort required to screen catalyst formulations for a given process, maximize the performance of their catalysts, and help establish a framework for the rational design of hierarchically structured porous catalysts at all length scales.

Coppens and co-workers have carried out extensive studies centered on the optimization of the micro/meso-macropore network of hierarchically structured catalysts, via mathematical and computational modeling, to reduce diffusion limitations [14,15] and mitigate the effects of catalyst deactivation by site poisoning and pore blockage [16,17]. They were able to show that introducing an optimized broad pore network characterized by uniform macroporosity and constant, optimal macropore size could significantly improve the volumetric reaction yield and increase the robustness towards catalyst deactivation, when compared with a purely micro/mesoporous (nanoporous) catalyst. As long as the porosity is sufficiently connected, they also demonstrated that introducing an optimized spatial and size distribution of macroporosity and macropore diameters did not lead to significant improvements over an optimized uniform macropore network, which is an important result from the standpoint of catalyst preparation. Keil and co-workers [18–21] employed both continuum and discrete pore network models to optimize the performance of hierarchically structured porous catalysts for industrially important reactions. While these studies have examined the optimization of hierarchically structured nano-macroporous catalysts, there has been no concerted effort to combine mathematical modeling and optimization studies with experiments. Secondly, given the vast body of literature focused on the synthesis of hierarchically structured zeolites [22–26], there is presently no work that provides guidance on the nature of the optimal pore structures for a given process, so that subsequent synthesis efforts can focus on producing the desired catalyst. Hence, there is a gap between materials chemistry and engineering in hierarchical catalyst design. As a step towards achieving the goal of rational catalyst design at all length scales, this work describes the numerical optimization of a hierarchically structured zeolite pellet to maximize the production of ethylbenzene in the ethylation of benzene over the acidic medium-pore zeolite H-ZSM-5 (a reaction chosen for reasons discussed further on), and compares the activity of different meso/macroporous zeolite composites in fixed bed reactor experiments with the numerically predicted performance of these catalyst pellets.

In addition, the topic of surface barriers in zeolite catalysis and their role in overall diffusion properties has also received increased attention, in part due to the availability of sophisticated characterization tools, such as interference and infrared microscopy [27,28] that allow for distinguishing the molecular uptake rates between different zeolite crystals synthesized in the same batch. Kärger and co-workers [29] have recently demonstrated that methanol uptake in single SAPO-34 crystals differs from one crystal to the other due to varying surface permeabilities; however, the uptake rates integrated over a large number of crystals in a batch can lead to the conclusion that intracrystalline diffusion rather than the surface barrier is rate limiting. Dauenhauer and co-workers [30,31] have also extensively investigated the importance of surface barriers for zeolite crystals using zero-length chromatography (ZLC), and have proposed that the adsorption of molecules from the gas phase on to the external surface of the zeolite crystal is characterized by a different rate constant than the rate of desorption of molecules from the external surface. Keil and co-workers [32–34]