

# Exploring Meso-/Microporous Composite Molecular Sieves with Core–Shell Structures

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**Abstract:** A series of core–shell-structured composite molecular sieves comprising zeolite single crystals (i.e., ZSM-5) as a core and ordered mesoporous silica as a shell were synthesized by means of a surfactant-directed sol-gel process in basic medium by using cetyltrimethylammonium bromide (CTAB) as a template and tetraethylorthosilicate (TEOS) as silica precursor. Through this coating method, uniform mesoporous silica shells closely grow around the anisotropic zeolite single crystals, the shell thickness of which can easily be tuned in the range of 15–100 nm by changing the ratio of TEOS/zeolite. The obtained composite molecular sieves have compact meso-/micropore junctions that form a hierarchical pore structure from ordered

mesopore channels (2.4–3.0 nm in diameter) to zeolite micropores ( $\approx 0.51$  nm). The short-time kinetic diffusion efficiency of benzene molecules within pristine ZSM-5 ( $\approx 7.88 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ ) is almost retainable after covering with 75 nm-thick mesoporous silica shells ( $\approx 7.25 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ ), which reflects the greatly opened junctions between closely connected mesopores (shell) and micropores (core). The core–shell composite shows greatly enhanced adsorption capacity ( $\approx 1.35 \text{ mmol g}^{-1}$ ) for large molecules

such as 1,3,5-triisopropylbenzene relative to that of pristine ZSM-5 ( $\approx 0.4 \text{ mmol g}^{-1}$ ) owing to the mesoporous silica shells. When Al species are introduced during the coating process, the core–shell composite molecular sieves demonstrate a graded acidity distribution from weak acidity of mesopores (predominant Lewis acid sites) to accessible strong acidity of zeolite cores (Lewis and Brønsted acid sites). The probe catalytic cracking reaction of *n*-dodecane shows the superiority of the unique core–shell structure over pristine ZSM-5. Insight into the core–shell composite structure with hierarchical pore and graded acidity distribution show great potential for petroleum catalytic processes.

**Keywords:** composite materials • core–shell structures • mesoporous materials • molecular sieves • zeolites

## Introduction

The focus of the present petroleum refineries is to effectively convert low-value heavy petroleum feedstocks to more valuable gasoline, middle distillates, and light olefins.<sup>[1]</sup> The major challenge for the present fluid catalytic cracking (FCC) process is the presence of bulky molecules in heavy feedstocks,<sup>[1b]</sup> and the diffusion of which during the catalytic reaction is hindered by the limited pore size of traditional zeolite materials (less than 1.3 nm).<sup>[2]</sup>

The commercial FCC catalysts are composed of active zeolites and silica–alumina-based matrices.<sup>[3]</sup> Generally, the matrices with large pores (i.e., macropores and mesopores) and a portion of acidity can participate in the overall cracking process and pre-crack partial heavy oil molecules.<sup>[3a, 4]</sup> Moreover, the large pores facilitate the capture of the bulky hydrocarbons, and thus alleviate the coke formation.<sup>[1c, 5]</sup> However, the matrices and zeolites in the FCC catalysts are mechanically mixed together, inevitably resulting in a random distribution of compositions and porous networks. On the other hand, the faujasite zeolite overgrown with a thin layer of mesoporous silica MCM-41 shows higher conversion of heavy products relative to naked ultra-stable zeo-

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