# Mass transport behavior in hierarchical porous materials revealed by frequency response method

**Lijuan Song,** * **Yucai Qin**
*Key Laboratory of Petrochemical Catalytic Science and Technology, Liaoning Province, Liaoning Shihua University, Fushun 113001, P.R. China*
**Corresponding author: lsong56@263.net*

**Abstract:** Utilization of hierarchical zeolites provides enhanced catalytic performance in several reactions, attributed to improved mass transport properties of reactant and product molecules. In this work, the frequency response method was applied to measure the mass transfer behaviors of guest molecules in series of zeolites and technical catalysts, and identify the rate-determining steps. It can be confirmed that the diffusion in the meso-/macro-pore in the matrix or/and at the zeolite-matrix interface are the controlling steps for the technical catalyst particles; and the molecules rearrangement processes in the pores or cages determine the mass transfer performance of zeolite crystals.
**Keywords:** Hierarchical zeolite, Mass transport, frequency response method, rate-determining step.

## 1. Introduction

The fundamental understanding of the mass transfer processes in hierarchical porous materials is essential for the development and tailoring of next generation adsorptive and catalytic materials[1,2]. The correlation between mass transfer and catalytic performance is one of the most challenging issues in heterogeneous catalysis. However, the overall mass transfer process constituted by a series of elementary steps is very complicated, and it has been unclear which step determines the overall transport process in hierarchical porous materials.

To resolve these contentious issues, the nature and role of the rate determining steps for the overall transport is addressed with diffusion studies using the frequency response technique, combining systematical texture characterization of the series of zeolite and technical catalyst materials. Some kinetic models containing all elementary steps involved in transport of the guest molecules from the gas phase to the sites inside the pores have been established via a detailed analysis of the experimental data.

## 2. Experimental (or Theoretical)

2.1 Experimental

A series of powdered zeolite (Y, ZSM-5, β, SAPO-34 etc.) and technical preformed catalysts (FCC and hydrocracking catalysts) were utilized as the research objects. The structure and texture properties of the samples were characterized by XRD, SEM, TEM, $N_2$ (77.4 K) and Ar (87.3 K) adsorption, and mercury intrusion method, etc.. Mass transfer behaviors of probe molecules (benzene, cyclohexane, octane, and 1-octene, etc.) in the samples have been measured and discriminated by the Frequency Response (FR) method and an Intelligent Gravimetric Analyser (IGA).

2.2 Theory of the FR

The pressure response can be mathematically described according to Yasuda by two characteristic functions (phase lag and amplitude). The phase lag $\Phi_{Z\text{-}B}=\Phi_Z-\Phi_B$, where $\Phi_Z$, and $\Phi_B$ are the phase angles determined in the presence and absence of sorbent, respectively. The amplitude ratio $P_Z/P_B$, is determined, where $P_Z$, and $P_B$, are the pressure responses to the ±1% volume perturbations in the absence and presence of sorbent, respectively[3].

The FR spectra, characteristic functions against frequency, which are derived from the equivalent fundamental sine-wave perturbation by a Fourier transformation of the volume and pressure square-wave forms, are described by the in-phase (real) and out-of-phase (imaginary) components, respectively.

## 3. Results and discussion

The FR technique has been used to study the mass transfer behaviors of several systems of the powdered zeolites and the technical preformed catalysts (*cf.* Figure 1). The results demonstrate the discrepancy in the mass transfer processes of benzene in the contrastive samples which just possess the different texture properties and crystal structures. It can be proved that the FR technique is a very sensitive one to investigate the effects of the texture properties and crystal structure on the adsorption and diffusion behaviors of the porous catalytic materials.

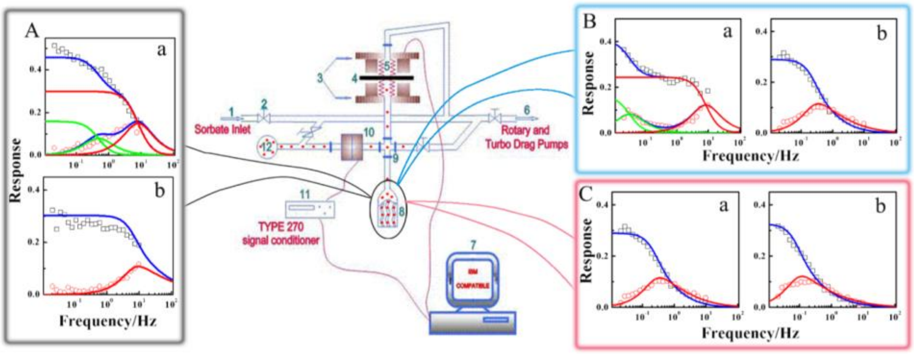


**Figure 1.** Schematic diagram of the FR equipment and the FR spectra of benzene in the samples used.
A: Y zeolites with micron-size (a) and nano-size (b); B: USY zeolite (a) and FCC catalyst particle (b); C: semi synthetic FCC catalyst (a) and in situ crystallization FCC catalyst (b).

The FR spectra demonstrate the differences in the mass transport processes of benzene in REUSY zeolite and the FCC catalyst particles under the same experimental situation. The discrepancy indicates that the controlling step for the overall molecular transfer processes in FCC catalyst particles might be attributed to the mass transfer process in the meso-/macro-pore in the matrix or/and at the zeolite-matrix interface rather than the intracrystalline diffusion in the zeolite. Comparing the FR results of two kinds of FCC catalysts, it can be seen that the in situ crystallization FCC catalyst displays more excellent mass transfer behavior than the semisynthetic FCC catalyst, which can be attributed to the excellent porous connectivity of the former with unique accumulation state of the highly dispersed nano Y zeolite crystals[4].

The discrepancy in the FR spectra of guest molecular in nano zeolites and the micron grade zeolite imply that the former one exhibit more excellent diffusion performance, which can be attributed to its unique texture properties and crystal structure. It can be confirmed that the essence of the improvement of mass transfer performance is the reduction of the effect of the molecules rearrangement process in the pores or cages which will restrict the molecule exchange process between inside and outside of the crystalline.

## 4. Conclusions

The FR technique is very useful to measure and distinguish the complex mass transport processes in hierarchical porous catalytic materials. This work provides some important guidances for the development and tailoring of next generation adsorptive and catalytic materials.

## References


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