

Investigation of diffusion properties of zeolite-based catalysts by inversion methods: principle and first applications

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The diffusion of reactants and products plays an important role in zeolite catalyzed reactions, where microporosity – while conferring exceptional catalytic properties – also imposes high diffusion limitations.¹ Diffusion properties are, however, rarely assessed in complex systems such as hierarchical or composite zeolite-based materials. In particular, classical macroscopic measurements of diffusion only provide diffusion parameters averaged over the whole material despite parallel diffusion domains. Further, they do not give information on the location of diffusing species (external surface / mesopores / micropores).

Here, we report the development and application of a new method of investigation of mass transport in zeolite-based materials aiming to overcome the limitations of classical approaches. It consists in hyphenating gravimetric analysis and infrared spectroscopy. The former allows assessing the diffusion from the gas phase to all the porosity, while IR allows for selective assessment of the diffusion to the zeolite active sites located in the micropores.² Further, these data are processed by an original methodology implemented in SpectroChemPy³ allowing to recover the distribution of diffusion domains by inversion of the integral equations describing the uptake curves or the evolution of the infrared spectra.

The general methodology was validated by evaluating the mass transport properties of isooctane in model bimodal systems consisting in mechanical mixture of H-MFI and H-FAU zeolites. As illustrated in Figure 1, the combination of gravimetric analysis and in situ IR makes possible to monitor and distinguish the diffusion within each component of the mechanical mixture. The inversion of the gravimetric uptake curve (a) leads to a distribution showing three diffusion domains (b). The inversion of the evolution of IR spectra (c), leads to a two-dimensional map (d) which also shows three species. Examination of their frequencies allows assigning the fastest domain to the H-FAU component and the two slow domains to the H-MFI component. Finally, the quantification and position of the corresponding peaks of the TG distribution (b) were consistent with the composition of the mechanical mixture and the diffusion rates measured in individual components, respectively.

After validation this methodology was applied to assess the impact of steaming on H-MFI zeolites in powder form or in form of extruded bodies. The results show that the relative values of diffusion rates as measured by gravimetry and IR spectroscopy are indicative of the quality of connectivity between meso and microporous networks. Besides the effect of the steaming treatment in zeolites, the influence of the nature of the binder and some preparation's parameters of the extruded catalyst was also evaluated.

In conclusion, the present methodology has the potential to provide unique insights into the assessment of diffusion properties of complex zeolite-based catalysts. Its limits, advantages and drawbacks with respect to conventional methods will be discussed.

References:

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