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NMR Imaging as a Tool for Studying the Diffusion and Co-Diffusion of Gases in Zeolite Catalysts

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1. Introduction

NMR imaging (MRI) technique was developed in the 70s mainly in the medical and biological fields. It involves at least one spatial coordinate.

Unfortunately, its relatively low spatial resolution makes it impossible to use it for studying microporous and even mesoporous materials at the length scale of the pore size. The best resolution achieved so far is of the order of a few microns. But MRI is useful for studying the diffusion of a gas through a permeable solid, in particular through a catalytic bed consisting of zeolites, not only to determine the diffusion coefficient of a gas, out of adsorption equilibrium, but also to determine the temporal evolution of the distribution of this gas in the bed. Finally and above all, it can be used to determine the evolution of the distribution in the solid of several gases diffusing competitively. This last point is particularly important in heterogeneous catalysis, since the rate of reaction between two reactants is generally proportional to the concentration of each one at each point in the catalytic bed.

We present here an application of this technique to the study of the diffusion of pure or mixed hydrocarbons (benzene, n-hexane) in a fixed bed of HZSM-5 zeolite during their adsorption at room temperature [1].

2. Experimental section

HZSM-5 zeolite was held under vacuum (10^{-5} mbar) at 673 K overnight before adsorption of gaseous hydrocarbon(s) at constant pressure at 293 K. At time $t = 0$ the sample is put into contact with the supply of liquid hydrocarbon (n-hexane or benzene) in equilibrium with the gas and is then placed quickly in the magnet. The liquid phase is either pure or consists of a mixture such that the two partial pressures of the gases are equal to 60 mbar. To distinguish the hydrocarbons when they are mixed, one is perhydro and the other perdeutero.

The proton 1D NMR images, which represent the concentration profiles of the hydrocarbons in the micropores along the samples (length: 5-15 mm), are recorded as a function of time (the concentration in the macropores is negligible).

3. Results

3.1: Adsorption of benzene or hexane.

At the very beginning of adsorption, ($0 < t < 0.1$ h) the 1D images of benzene adsorbed in the powder HZSM-5 bed show a strong concentration gradient decreasing from the top to the bottom of the sample. When $t > 0.2$ h, rectangular profiles are obtained proving that after this time the benzene concentration is the same in any part of the bed and that the diffusion is then controlled by the micropores. This experiment allows the determination of D_{intra} (1×10^{-14} m^2 s^{-1}). In the case of n-hexane the concentration profiles become perfectly rectangular after only $t = 0.03$ h; $D_{\text{intra}} \approx 10^{-13}$ m^2 s^{-1}.

4. Diffusion of gas mixture (benzene + hexane).

Different types of experiments were performed: *i*) their competitive adsorption, *ii*) the variation of the distribution of a pre-adsorbed hydrocarbon during the adsorption of a second one. We report here the first case (Figure 1).

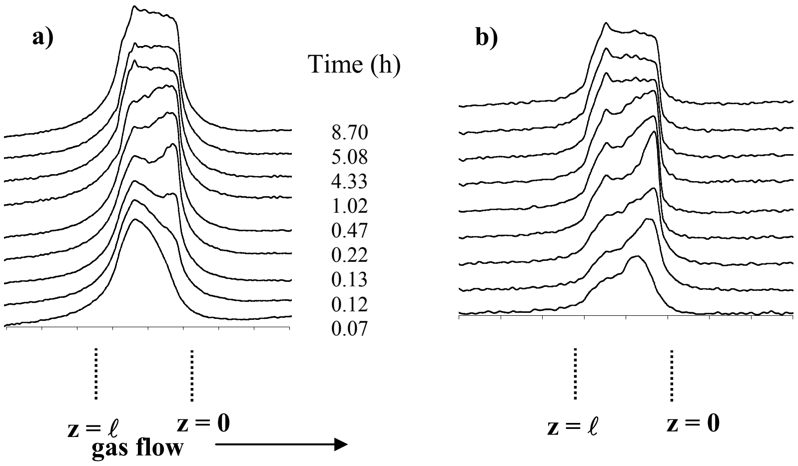

Fig. 1. 1D-NMR profiles of n-hexane a) and benzene b) during their competitive adsorption in HZSM-5 zeolite.

These profiles clearly show that benzene first adsorbs preferentially in the bottom layers before displacing the n-hexane adsorbed in the top layers and finally the equilibrium is reached over the entire sample.

5. Conclusion

The application of ^{1}H 1D-MRI for the study of hydrocarbon diffusion gives two types of information. First, the variation with time of the surface area of the full signal during adsorption makes it possible to determine transport coefficients by simulation of the kinetic curves. Second, the shape of the instantaneous concentration profiles reflects the variation of the local adsorbate concentration, and reveals a competition between kinetic and thermodynamic effects.

6. References

[1] P.N'Gokoli-Kekele, M-A. Springuel-Huet, J-L. Bonardet, J-M. Dereppe, J. Fraissard. Proceedings of the 13th Int. Zeolite Conference, Montpellier,2001