Probing diffusional exchange in mesoporous zeolite by NMR diffusion and relaxation methods.

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Résumé

We propose NMR relaxation techniques to evaluate diffusional exchange between the different porosity compartments of heterogeneous catalyst extrudates in addition to NMR diffusion measurements. The two systems considered are close to industrial products and contain a wide distribution of pore sizes spanning from microporosity (2 types of zeolites CBV400 and CBV720), mesoporosity induced by the alumina binder, and macroporosity introduced during the shaping procedure. The question is to determine in which system the meso and macroporosity provide the best access to microporosity. Beside standard techniques, we measured the pore size distribution using NMR cryoporometry in the range 2nm up to 1 μm, and the amount of microporosity below 2 nm from relaxation data at -29$\circ$C. These measurements provide reference values independently of the connectivity or the hierarchical organization of the pore network. Long range diffusion was measured using methane and cyclohexane to evaluate the effect of macropores. When saturated with squalane, the diffusive exchange between micro and mesoporosity was evaluated using two techniques: (i) the comparison of the apparent mesoporosity fraction in the T2 distribution to the true value measured by cryoporometry, (ii) the measurement of exchange times using T2-exchange-T2 experiments. These two approaches give coherent results. The diffusive coupling was also observed with 2-propanol saturated extrudates, for which the surface residence time tS was evaluated from the interpretation of the 3 relaxation times T2, T1 and T1r; for the 2 samples tS differ by 2 orders of magnitude due to the very different Si/Al ratio of the 2 zeolites used in the extrudates. All these methods lead to the conclusion that the presence of mesoporosity in zeolite crystals is beneficial to the diffusive transport with the surrounding porosity only when molecule/zeolite interactions are not predominant.

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