Abstract submitted on line to Interpore 2021 Annual Meeting 31 May-4 June

"Beyond tortuosity: evaluating connectivity in multimodal catalysis supports"

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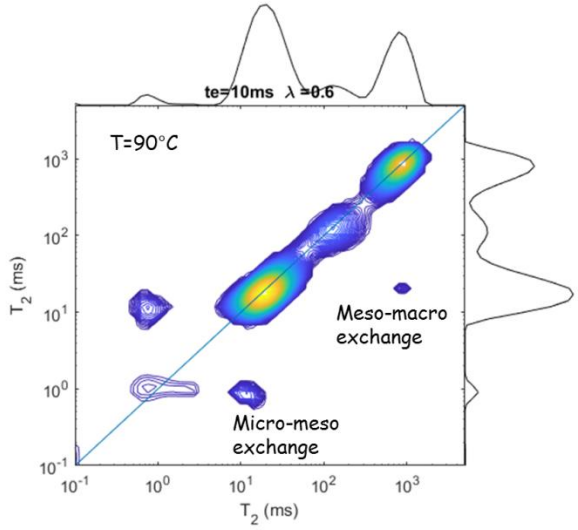
The diffusion properties are a key parameter for catalysis supports. These properties are often gathered in one single parameter called tortuosity defined as the ratio of the bulk to the effective diffusivity on a given liquid or gas diffusing inside the porous media. The tortuosity parameter is expected to depend on the geometry of the porous network without chemical interaction of the molecules with the solid surface. However, for complex composite support materials comprising, for example, microporous zeolites and mesoporous oxide binders, the tortuosity concept is not sufficient for describing the transport properties as it might also depend on pore size, type of liquid and surface properties [1–4]. More detailed information about the connectivity between the different pore compartments and the limiting transport steps is needed. In this work we deal with hydrocracking catalysts supports as a study case. These systems contain a wide distribution of pore sizes spanning from microporosity (2 types of zeolites), 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.

For this purpose, we used various NMR techniques at low field: NMR cryoporometry to determine pore size distribution in the range 2 nm to 1 micron and the amount of microporosity [5,6], standard PFG-NMR to determine diffusion coefficients, T1 and T2 relaxation time distribution and relaxation exchange spectroscopy (REXSY [7]) to evaluate diffusive exchange between porous compartments. Different fluids were used: water, cyclohexane, squalane and 2-propanol. We varied also the temperature up to 90°C. Diffusive exchange is best revealed in T2-exchange-T2 maps (see figure) when the diffusion length is limited or when the solid-liquid interactions are strong, for example using squalane or 2-propanol respectively. The analysis of these maps allows quantifying the exchange time and compare catalysis supports in terms of diffusive transport, in addition to tortuosity.

The two studied samples labeled A and B vary essentially by the nature of zeolite used. A and B have respectively a specific surface of 843 and 727 m^2/g. The measured exchange time (with squalane) between micro and mesoporosity was similar for both A and B, but the relative amount of exchanged molecules was larger for B. Hence while B is less porous and slightly more tortuous with a smaller surface, it has better local transport properties than A. The relation between the transport properties of these hierarchical systems and the characteristics of the zeolites constituting A and B will be analyzed in detail.



Example of T2-exchange-T2 map performed on one catalysis support saturated with squalane, performed at 90°C for an exchange time of 10 ms. The off-diagonal peaks reveal the diffusive exchange between micro, meso and macro-porosity compartments.

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