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Study of the Butane Diffusion in Metal Organic Framework Materials by PFG NMR Experiments.

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1. Introduction

The presence of organic part in the new class of hybrid solids imparts an important chemical versatility to these materials compared to "classical" solids. The architecture of Metal Organic Frameworks (MOF) may lead to open structures with 1D (chains), 2D (layers) or 3D dimensionality developing very large surface areas (above 1000 m^2/g) [1]. Some MOFs possess a structural originality: the frameworks are flexible and movements larger than 10 Å can be generated in response of external stimuli (temperature, adsorption of guest molecules). It is therefore interesting to explore the diffusion properties of these materials.

The present work reports the study by Pulsed Field Gradient (PFG) NMR of the diffusion of butane in two hybrid solids, named MIL-53 (Ga)and MIL-103 (La), MIL standing for "Institut Lavoisier Materials". The structure of MIL-53 and MIL-103 consists of chains of octahedral metal ions (Ga, La, respectively) connected by organic linkers (benzene dicarboxylate, benzene tribenzoate, respectively) forming 1D channels with 8.6 Å and 10 Å pore diameter, respectively [2,3].

2. Materials and Methods

The crystal shape is plate for MIL-53 (Ga) and needles for MIL-103 (La) and presenting mean crystal sizes of ca. 150×50×20 μm and 10×1×1 μm, respectively.

The adsorption isotherms of butane measured at 295K using a home-built system have a rectangular form typical of alkane-zeolite systems for both samples. The samples were carefully dehydrated at 423 K under vacuum and filled with a quantity of butane corresponding to the saturation. The measurements of self-diffusivities were performed on a Bruker DSX spectrometer at a ^1H resonance frequency of 300 MHz equipped with a Bruker Diff30 probe delivering a maximum gradient, g, of 12 $T.m^{-1}$. The value of the observation time, Δ, was chosen in the range of 6 to 12 ms. In order to eliminate the contribution of the internal field gradients, the PFG NMR measurements were carried out using the 13-interval bipolar pulse sequence [4].

3. Results and discussion

The attenuation curves , $\ln(\psi)$ versus g^2, obtained for butane in both samples show two distinct parts corresponding to two types of diffusing molecules. The slope of the linear part at high field gradient allows us to determine the diffusivity of molecules inside the particles during the whole observation time which depends on the observation time suggesting the occurrence of a restricted diffusion inside the particles [5].

The model developed by Mitra et al. [6] was used to determine the intracrystalline diffusivity and the surface-to-volume ratio, S/V, of the region of restricted diffusion.

Data are given in the Table. The diffusivities of butane in both samples are similar. This might be a consequence of the similar diameters, 8.6 - 10 Å of the 1D channel pore.

For MIL-103, the S/V ratio is similar to the surface-to-volume ratio, calculated from the particle dimensions, which is in favour of monocrystalline particles letting the butane molecules diffuse freely in the entire crystals.

For MIL-53, the experimental S/V ratio is at least ten times greater than the calculated value. Then, the domains of restricted diffusion are much smaller than the particle itself and the butane molecules can not diffuse freely in the whole of these particles. Therefore, the MIL-53 particles probably consist of small monocrystalline domains.

Table 1. D_{intra}, calculated and experimental S/V ratios and mean lifetime, τ_{intra},

Samples	Particle size[a]	D_{intra} ($m^2.s^{-1}$)	S/V_{calc}.	S/V_{exp}.	τ_{intra} (ms)
MIL 53 (Ga)	(150×50×20×µm) [a]	1.6×10^{-10}	2×10^{5}	3×10^{6}	4
MIL 103 (La)	(10×1×1µm)[a]	2.1×10^{-10}	4×10^{6}	3×10^{6}	7

[a] Average particle size from electron microscopy images

To better understand the diffusion behaviour of adsorbed molecules, the mean lifetime, τ_{intra}, of a molecule inside a particle can be calculated by integrating the fraction of molecules remaining in the intraparticle space during the observation time, a(Δ) [7].

Due to smaller particle size in MIL-103, one would expect smaller τ_{intra} values in MIL-103 than in MIL-53 unlike what is obtained. The comparison of τ_{intra} values suggests that the monocrystalline domains in MIL-53 are slightly smaller than the MIL-103 particles.

4. Conclusion

The diffusion of butane has been studied by PFG NMR in new hybrid materials MIL-53 and MIL-103. The self-diffusivities depend on the observation time revealing a restricted diffusion of the molecules. The comparison of the S/V ratio and τ_{intra} values shows that the large MIL-53 particles are not monocrystalline but consist of an assembly of smaller monocrystalline domains. On the contrary, the MIL-103 sample seems constituted of monocrystalline particles from the point of view of diffusion.

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