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Diffusion Studies on Large-Crystal Ferrierite Zeolites of Different Chemical Composition and Post-Synthesis Treatment

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1. Introduction

The potential to record the evolution of intra-particle concentration profiles in transparent nanoporous materials with interference (IFM) and IR microscopy (IRM) has opened a new field of diffusion research [1]. The high spatial and temporal resolution of both techniques does not only enable the determination of accurate (transport-) diffusivity values, but also the observation of transport barriers inside the studied material and on the material surface and therefore the determination of the actual path the guest molecules take on their way into the porous material.

The capabilities of both techniques to monitor mass transport and to observe transport hindrances are illustrated exemplarily in recent sorption experiments of short hydrocarbons in large ferrierite crystals. We studied the uptake and release of methanol, ethanol, ethane, ethylene, propylene and propane at room temperature in all-silica and aluminium-containing ferrierite crystals, which were just calcined or calcined and NaOH-etched before the experiments.

2. Experimental Results

Figure 1 provides an overview of the obtained results, which may be summarized by the following conclusions:

(1) Large transport barriers are located at the entrances of the 10-ring channels of the only-calcined crystals, leading to a quasi-one-dimensional (and therefore retarded) uptake process along the 8-ring channels of the crystals.

(2) These surface barriers can be reduced by etching the crystals with NaOH. After the NaOH treatment, both the 8- and 10-ring channels are accessible for mass transport via the surface of the crystals.

(3) The diffusion of the studied molecules in ferrierite is anisotropic. The molecules diffuse faster in the 10-ring channels than in the 8-ring channels. The extent of the observed anisotropy depends on the chemical composition of the crystal and is higher in all-silica crystals than in aluminium-containing crystals.

(4) The mobility of the studied molecules decreases dramatically with increasing molecular diameter. The diffusivities of methanol and ethanol along the 10-ring channels differ e.g. by as much as six orders of magnitude.

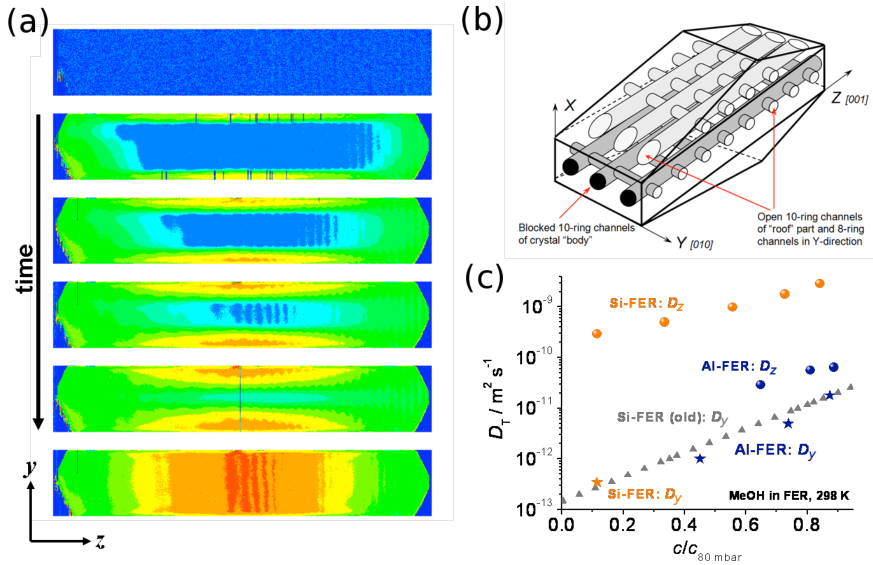

Figure 1: (a) Uptake of methanol in a NaOH-washed all-silica ferrierite crystal. The profiles clearly indicate fast transport along the 10-ring channels which were opened by the NaOH-washing. (b) Schematic illustration of the pore structure in ferrierite crystals. (c) Transport diffusivities for methanol in 8- and 10-ring channels of all-silica and aluminium containing ferrierite (reference data *Si-FER (old)* taken from [2]).

3. Conclusion

Summing up, by studying the impact of different post-synthesis treatments on molecular uptake a washing step could be identified to opens the previously blocked pores for guest uptake, leading to remarkably enhanced uptake rates. Comparison of the diffusivities of different molecules provided a first insight into the potentials of ferrierite for separating molecule mixtures, notably of short paraffins/olefins and of small alcohols.

References

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