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PFG NMR Measurement of Molecular Diffusion in Cation-Free Zeolites of Type LTA

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1. Introduction

In elucidating the origin of the discrepancies in the message of different experimental techniques on intracrystalline diffusion in zeolites, theoretical approaches correlating the rate of translational migration with the potential fields exerted by the zeolite framework on the diffusing molecules have attained particular relevance. Due to some residual ambiguity in the theoretical approaches for the cation-sorbate interaction, in this way especially weighty evidence is provided in the case of cation-free zeolitic adsorbate-adsorbent systems. The comparison of experimental diffusion studies with the results of molecular simulations for n-alkanes in silicalite-1 is a prominent example of such investigations [1]. Though to a considerable extent MD simulations have been devoted to molelcular diffusion in cation-free LTA [2, 3], only with the recent advent of this material with crystal sizes of the order of 10 to 20 µm [4] genuine experimental studies with this important type of material has become possible. We are going to present the first results of PFG (pulsed field gradient) NMR diffusion measurements with cation-free, purely siliceous LTA.

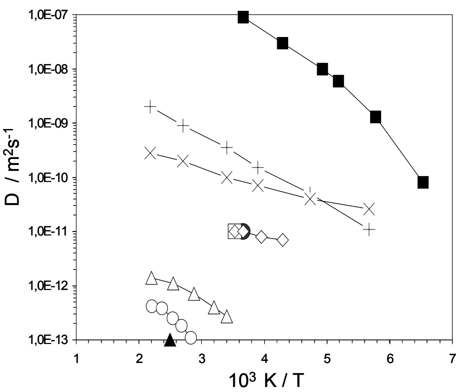

Fig. 1 Self-diffusion coefficients of (+) methane, (x)ethane, (Δ)propane [7], and of (○)methanol [8] in NaCaA in comparison with the first results obtained with two different specimens of cation-free Si-LTA, viz. of (■)ethane and (▲)propane in specimen I and of (□)ethane, (◇)ethene and (●)methanol in specimen II.

2. Experimental and results

Two specimens of cation-free Si-LTA zeolite were synthesized and found to be of genuine LTA structure type by x-ray diffraction analysis. PFG NMR samples were prepared in the conventional way as described in [5]. The PFG NMR measurements were performed at the home-built spectrometer FEGRIS 400 NT at a proton frequency of 400 MHz by means of the 13-interval pulse sequence [6].

In fig. 1 the diffusivities of this study are represented together with previous PFG NMR data obtained for the n-alkanes [7] and methanol [8] adsorbed in NaCaA. The obtained data may be rationalized by implying the existence of pronounced intracrystalline transport barriers (such as fault planes evidenced, e.g., in [5, 9, 10] which act in addition to the intracrystalline bulk phase and whose intensity may vary between different batches of synthesis. In this way it may become plausible that in specimen I the ethane diffusivity is much larger than in NaCaA (as to be expected for the cation-free adsorbent; in fact these diffusivity data do even refer to long-range rather than intracrystalline diffusion), while in specimen II - presumably as an effect of the intracrystalline transport resistances, obviously more strongly developed in this batch of synthesis - the diffusivities are reduced. Since in the cation-free sorbent differences in the polarity should be of minor influence, it is not unexpected that the diffusivities of ethane, ethene and methanol are comparable, exceeding, e.g., decisively the diffusivity of methanol in NaCaA. Again, in view of the increased critical diameter not unreasonably, the further drop in the diffusivity of propane may be referred to an enhanced influence of the internal barriers in the cation-free LTA.

3. Conclusion

First PFG NMR measurements of molecular diffusion in cation-free zeolites of type LTA are presented. For rationalizing the results the existence of intracrystalline transport resistances has to be implied. It has to be clarified in further studies up to which extent under such conditions information about the rate of molecular migration under the influence of the genuine LTA framework may be deduced.

References

[1] L.N. Gergidis, D.N. Theodorou, H. Jobic, J. Phys. Chem. B. 104 (2000) 5541.
[2] P. Demontis, G.B. Suffritti, J. Phys. Chem. B. 101 (1997) 5789.
[3] A. Schüring, S.M. Auerbach, S. Fritzsche, R. Haberlandt, J. Chem. Phys. 116 (2002) 10890.
[4] A. Corma, Nature, 431 (2004) 287 - 290.
[5] H. Jobic, H. Paoli, A. Methivier, G. Ehlers, J. Karger, C. Krause, Microporous and Mesoporous Mat. 59 (2003) 113.
[6] P. Galvosas, F. Stallmach, G. Seiffert, J. Kärger, U. Kaess, G. Majer, J. Magn. Reson. 151 (2001) 260.
[7] W. Heink, J. Kärger, H. Pfeifer, P.Salverda, K.P. Datema, A.K. Nowak, J. Chem. Soc. Faraday Trans. 88 (1992) 515 - 519.
[8] U. Schemmert, J. Kärger, C. Krause, R.A. Rakoczy, J. Weitkamp, Europhys. Lett. 46 (1999) 204.
[9] S. Vasenkov, W. Böhlmann, P. Galvosas, O. Geier, H. Liu, J. Kärger, J. Phys. Chem. B. 105 (2001) 5922.
[10] J.R. Agger, N. Hanif, C.S. Cundy, A.P. Wade, S. Dennison, P.A. Rawlinson, M.W. Anderson, J. Am. Chem. Soc. 125 (2003) 830.