



ELSEVIER

Journal of Molecular Catalysis A: Chemical 166 (2001) 167–174



www.elsevier.com/locate/molcata

Dynamic behaviour of azonia-spiro-alkanes within the MOR and MTW zeolite pore structures

Francesco Frigerio*, Luciano Carluccio, Wallace O'Neil Parker Jr., Roberto Millini

EniTecnologie S.p.A. Via F. Maritano 26, I-20097 San Donato, Milanese (MI), Italy

Abstract

The molecular packing stability and the dynamic behaviour of three azonia-spiro-alkanes involved as structure determining agents in the zeolite synthesis has been examined in the frameworks of MOR and MTW. A detailed molecular model has been set up by computer graphics methods and used to perform Monte Carlo packing and molecular dynamics simulations. The energetic stabilisation and molecular mobility have been calculated and compared to previous experimental characterisation data. The results are found useful to discuss the packing preferences of this class of molecules in the zeolite pores under investigation, with the aim of rationalising their templating ability and selectivity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molecular dynamics; Monte Carlo; Zeolite; Template; Mobility

1. Introduction

The design of new mesoporous materials with desired structural characteristics requires a detailed understanding of the templating role of organic additives in the zeolite crystallisation [1]. Their influence on the product frameworks is strongly related to the synthesis conditions (e.g. gel composition, temperature, pH) while the nature of the crystalline products depends on the size, shape and conformation of the organic additives, but generally no influence is due to their chemical character [2]. Since a strict correlation between the molecular shape of the additive and the surrounding zeolite cage environment is implied in the definition of a template, they can be indicated more appropriately as structure-directing agents (SDA). In our laboratories, the application of the azonia-spiro-alkanes (ASK) I, II,

III (Fig. 1) to different experimental conditions led to several known framework structures (MOR, MTW, β , EUO, EU-4) and a new microporous phase (ERS-10 [3]). Our efforts are aimed at the evaluation of the potential templating ability of a series of homologous molecules in similar experimental conditions, in order to select the most promising SDAs for the synthesis of a specific zeolite framework.

A molecular modelling approach has been applied to the rationalisation of the shape and energy requirements that drive the zeolite synthesis in the presence of SDA molecules. The produced zeolites are generally characterised by relatively large and linear pores, that seem well suited to accommodate the cylindrically symmetrical SDAs used in the synthesis. On the other hand, the SDA selectivity displayed in the adopted conditions is rather low. In a previous work [4] the SDA compatibility with the framework was correlated with the normalised binding energy (BE*) calculated by Monte Carlo docking and energy minimisation of a single ASK molecule in the pores of MOR and MTW.

* Corresponding author. Tel.: +39-0252-056-443;
fax: +39-0252-036-347.
E-mail address: ffrigerio@enitecnologie.eni.it (F. Frigerio).

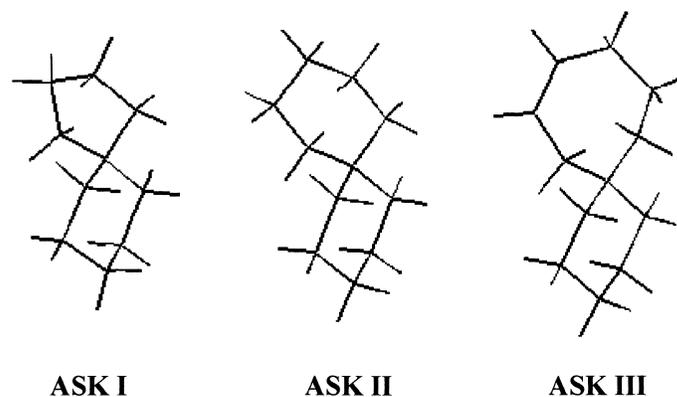


Fig. 1. The molecular structure of ASK I, II, III (respectively, 5-azonia-spiro-[4,5]-decane, 6-azonia-spiro-[5,5]-undecane, 6-azonia-spiro-[5,6]-dodecane) is depicted in extended conformation.

A more accurate computer model of the ASK/zeolite configurations is now proposed in order to study some properties of the system. The measured difference of SDA occupancy in MOR and MTW can be interpreted by testing the maximum feasible ASK packing in the zeolite pores. In the interpretation of NMR spectra [4] the peculiar steric requirements of each zeolite framework were proposed to have an influence on the ASK mobility. This can be studied by examining the trajectories of molecular simulations reproducing, as far as possible, the experimental conditions. It was suggested that SDAs can properly affect the zeolite synthesis when favourable non-bonding interactions between the SDAs and the framework are maximised and an efficient host/guest packing is obtained [5]. The multiple docking stabilisation of the ASKs and their mobility in the MOR and MTW pores were, therefore, evaluated with reasonable approximations by a simulation procedure combining Monte Carlo packing (MCP) and molecular dynamics (MD).

2. Computational details

A computer model of the specific ASK/zeolite interactions was built in a previous study [4]. Values for the binding energy (BE^*) were calculated by single molecule Monte Carlo docking and correlated with the observed low selectivity of the ASK ions in the zeolite synthesis. The model is here extended to include the molecular packing effects of the ASKs I, II, III in

the frameworks of MOR [6] and MTW [7]. The atom coordinates were built within InsightII [8]. The pccf forcefield, validated for both organic polymers and zeolites [9], periodic boundary conditions and the Ewald summation method were adopted. The molecular simulations were performed and analysed on a SGI Indy workstation with the Catalysis 4.0.0 [8] and Discover 3 [8] programs. The main simplifying assumptions adopted were: fixed, purely siliceous zeolite frameworks, neglect of the coulombic interactions [5], absence of solvent molecules and counterions.

The zeolite pore volume available to the filling procedure (V_{free}) was evaluated by means of a sphere with radius of 1.45 Å, corresponding to the average volume occupied by one ASK non-hydrogen atom. The maximum molecular packing ability of the ASKs was tested by a MCP procedure. A fixed number of ASK molecules was randomly inserted in the empty pores of each zeolite model, until a representative set of acceptable configurations (i.e. below a predefined energy limit) was produced, then the potential energy was minimised. These calculations were repeated with an increasing number of ASK molecules and the lowest potential energy components were plotted for each of the configuration sets. The molecular packing densities of ASK I, II, III in the MOR and MTW pore systems that were adopted for the MD simulations are based on the occupancy measured by the thermogravimetric analysis [4]: five ASK molecules in the MOR supercell built with 1·1·3 translations (MOR113); nine ASK molecules in the MTW

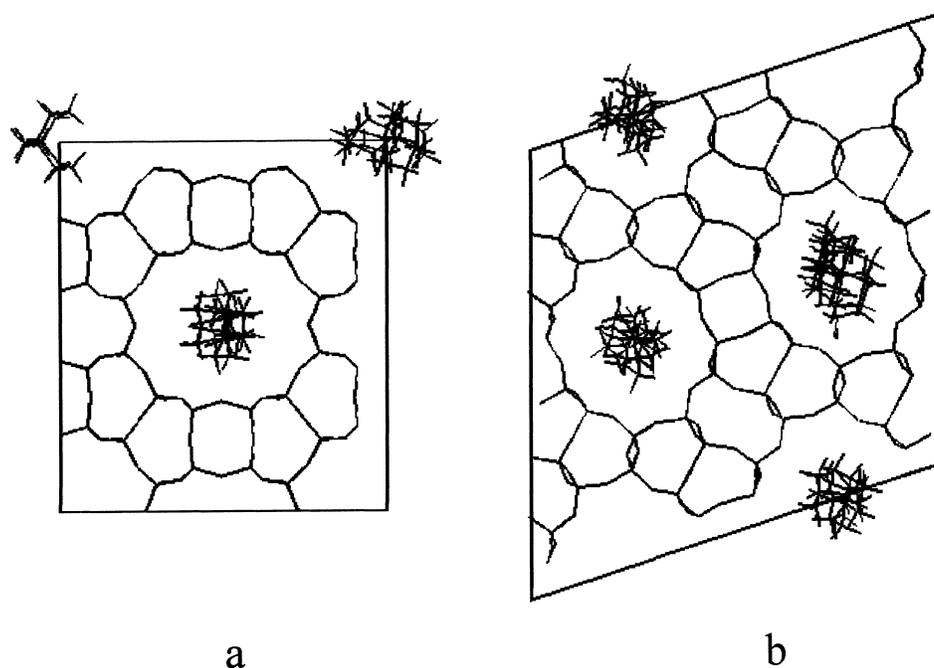


Fig. 2. The five ASK/MOR113 (a) and nine ASK/MTW141 (b) configurations adopted for the MD simulations are depicted for ASK II.

supercell with 1·4·1 translations (MTW141), approximately corresponding to 1.7 and 2.3 molecules per unit cell (Fig. 2). Three sets of zeolite-free systems were built for comparison: a single ASK in an orthorhombic cell (EC, dimensions of 18.1 Å × 20.5 Å × 22.6 Å, the same as MOR, but with P1 symmetry); five ASKs in a cubic cell (TCMOR, $a = 14.0$ Å and P1 symmetry, volume = V_{free} for MOR); nine ASKs in a cubic cell (TCMTW, $a = 13.6$ Å, P1 symmetry, volume = V_{free} for MTW).

All ASKs were initially subjected to 10 ps MD in vacuo at 1000 K, then to MCP and energy minimisation. The lowest potential energy configuration was selected for each ASK/framework assembly as the starting coordinates for the subsequent simulations. All MD simulations were conducted in the NVT canonical ensemble, at the temperature of 300 K, with a time step of 0.5 fs, ABM4 velocity integrator and the Nosè temperature control method. After an initial equilibration step of 1 ps, every assembly was subjected to a 100 ps data collection run. The atomic coordinates and velocities and the energy components were saved every 1 ps. For each of the studied sys-

tems, some additional 50 ps MD runs were produced, with the same parameter set and starting coordinates, but with different initial velocity distributions.

3. Results and discussion

The molecular models adopted for MD in this study account for the experimental loading of the ASKs I, II, III in MOR and MTW. However, MOR113 and MTW141 share a comparable free volume (V_{free}) of the empty pores, therefore a different number of packed ASKs produces an efficient volume filling in MTW141, but a lower occupancy in MOR113, as indicated by the V_{free} values calculated after packing (Table 1). A visual inspection of the small lateral cavities along the MOR pores suggests that they are scarcely available to molecules as large as the ASKs. In order to test this observation, a MCP evaluation of the ASK maximum packing in MOR and MTW was run. The docking procedure was able to fit 12 ASK molecules in both the MOR113 and the MTW141 pores (but not more than nine ASK III in MTW141).

Table 1

Volume (\AA^3) available in MOR113 and MTW141, before and after being packed with ASKs I, II, III, calculated with a sphere of radius 1.45 \AA

Zeolite	MOR113			MTW141		
V_{cell}	8379			11552		
$V_{\text{free of the empty zeolite pores}}$	2752			2532		
	ASK			ASK		
	I	II	III	I	II	III
ASK atoms (non-H)	140 (50)	155 (55)	170 (60)	252 (90)	279 (99)	306 (108)
$V_{\text{occupied (by ASKs only)}}$	698	770	832	1062	1188	1313
$V_{\text{free (after packing)}}$	1371	1274	1180	346	77	79

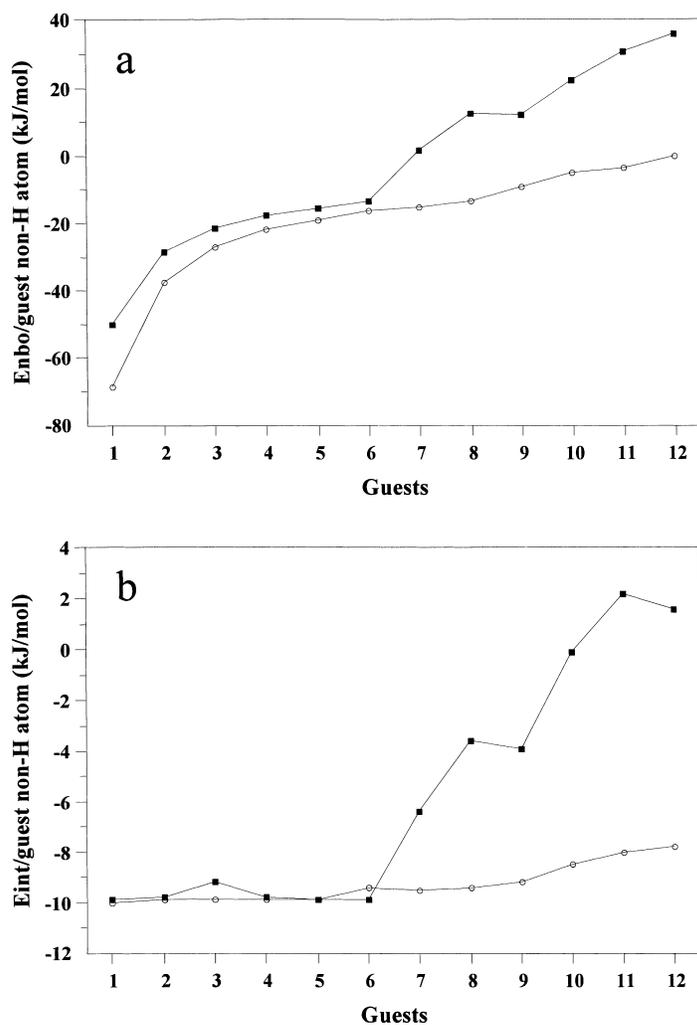


Fig. 3. Plots of the non-bonded (a) and internal (b) contributions to the potential energy (normalised by the number of ASK molecules and non-H atoms) calculated for the multiple docking of 1–12 ASKs II in the MOR113 (■) and the MTW141 (○) pores.

Table 2

Energy components (kJ mol^{-1}) for the ASK I, II, III packed configurations in MOR113 and in MTW141 (normalised by the number of non-hydrogen ASK atoms)^a

Cell ^b	MOR113			MTW141		
	ASK			ASK		
	I	II	III	I	II	III
TOT*	1.62	-2.53	0.08	2.78	2.31	5.56
KIN*	10.48	10.55	10.61	10.48	10.55	10.61
POT*	-8.87	-13.08	-10.52	-7.70	-8.24	-5.05
NBO*	-13.91	-13.34	-12.09	-12.36	-9.70	-7.16
INT*	5.04	0.26	1.57	4.66	1.47	2.10
BE*	-8.82	-7.31	-6.40	-8.36	-7.28	-7.01

^a The binding energies (BE*) calculated with the Monte Carlo docking of a single ASK in MOR and MTW [4] are reported as reference.

^b TOT*: total; KIN*: kinetic; POT*: potential; NBO*: non-bonded; INT*: internal.

The energy minimisation of the packed configurations revealed that the energy cost of multiple ASK insertion is different in the two zeolite pore systems, as pointed out, for example, by the results for ASK II (Fig. 3). Both the non-bonded and the internal energy contributions to the potential energy are negative for all multiple ASK packing configurations in MTW141. On the contrary, in MOR113 the cost for the insertion of more than six ASKs results in positive values for the non-bonded potential energy of the system. The degree of conformational distortion imposed by the zeolite pore structures is clearly evidenced by the internal energy values. A horizontal trend is observed until nine ASKs are packed in MTW141, followed by a smooth increase, while the corresponding values

Table 3

Energy components (kJ mol^{-1}) for the ASK I, II, III configurations in the zeolite-free cells TCMOR, TCMTW and EC (normalised by the number of non-hydrogen ASK atoms)

Cell	TCMOR			TCMTW			EC		
	ASK			ASK			ASK		
	I	II	III	I	II	III	I	II	III
TOT*	16.18	12.30	13.36	13.73	10.18	11.11	18.04	14.65	15.95
KIN*	10.41	10.48	10.54	10.44	10.51	10.57	10.11	10.21	10.30
POT*	5.77	1.81	2.82	3.29	-0.34	0.55	7.93	4.44	5.65
NBO*	0.70	1.33	1.38	-1.44	-0.86	-0.55	3.38	4.18	4.55
INT*	5.07	0.49	1.44	4.73	0.52	1.09	4.55	0.26	1.10

Table 4

Differences between energy components (kJ mol^{-1}) of Tables 2 and 3^a

Cell	MOR113			MTW141		
	ASK			ASK		
	I	II	III	I	II	III
$\Delta 1\text{POT}^*$	14.63	14.89	13.34	10.99	7.90	5.60
$\Delta 1\text{NBO}^*$	14.61	14.67	13.47	10.92	8.84	6.61
$\Delta 1\text{INT}^*$	0.03	0.23	-0.13	0.07	-0.94	-1.01
$\Delta 2\text{POT}^*$	16.80	17.51	16.18	15.63	12.67	10.70
$\Delta 2\text{NBO}^*$	17.29	17.52	16.64	15.74	13.89	11.71
$\Delta 2\text{INT}^*$	-0.49	-0.01	-0.47	-0.11	-1.21	-1.01

^a $\Delta 1 = (\text{MOR113} - \text{TCMOR})$ or $(\text{MTW141} - \text{TCMTW})$, $\Delta 2 = (\text{MOR113} - \text{EC})$ or $(\text{MTW141} - \text{EC})$.

calculated for the MOR113 configurations steeply rise after six ASKs. Very similar observations can be done with the energy values calculated for the configurations involving the other two ASKs (with an increased difficulty to accept high packing values in the case of ASK III). Due to the solvent neglect in the MCP procedure, slightly tighter packing is found feasible in both zeolite models, compared to experiment, but still in good agreement with the TGA results [4].

The total, kinetic and potential energies (broken into non-bonded and internal contributions) of the configurations collected along the MD trajectories were averaged and normalised by the number of non-hydrogen ASK atoms (Tables 2 and 3). The potential energies (POT*) indicate a preference for the molecular packing of ASK II over I and III, while all three ASKs sit better in the framework of MOR rather than in MTW. The following order of stability is produced in the MD conditions: ASK II > III > I (in MOR113,

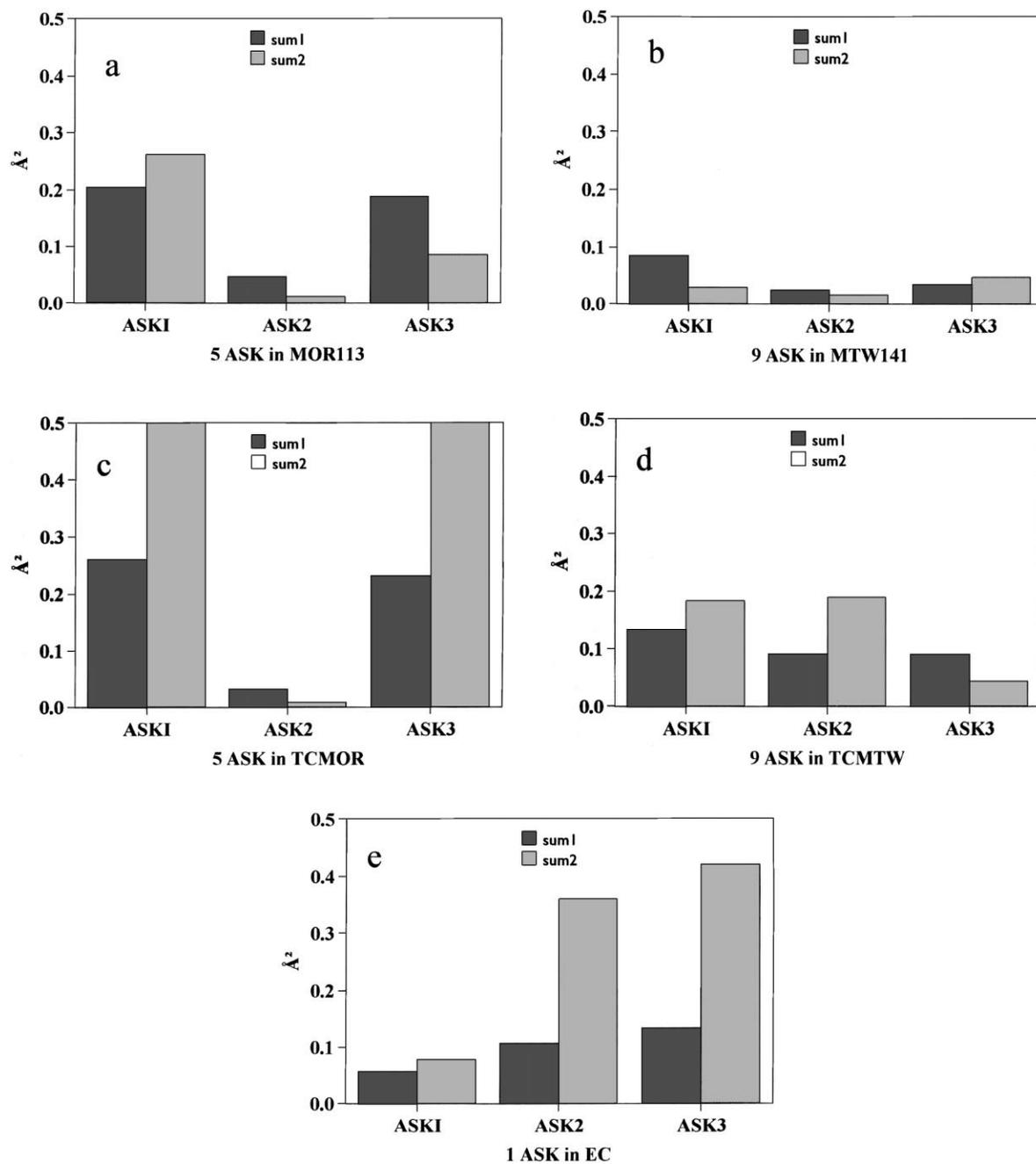


Fig. 4. MSD for ASK I, II, III in the MOR113 and MTW141 zeolite cells and the TCMOR, TCMTW and EC zeolite-free cells, calculated from the MD trajectories, FFT filtered and reported as the sum of average values for frequencies higher (sum1) and lower (sum2) than 5 cm^{-1} .

TCMOR and TCMTW) and ASK II > I > III (in MTW141). However, in all the simulated packing systems the non-bonding contribution to the potential energy (NBO*) becomes less favourable with increasing the ASK molecular size: I > II > III. The same was found for the binding energies (BE*) calculated by Monte Carlo single molecule docking [4]. More favourable values for MOR113 are possibly due to the lower ASK occupancy, allowing an overall tighter packing in the best docking sites, as compared to MTW. In all packing systems the INT* values follow the order ASK II > III > I.

The stabilisation due to ASK packing can be evaluated by the difference in the energy contributions calculated for the multiple ASK/zeolite configurations and for the single ASKs in the EC zeolite-free cell (Table 4). The $\Delta 2\text{NBO}^*$ values indicate highly favourable molecular packing for all three ASKs, as well as a decreasing trend, more evident in MTW141, with increasing the ASK molecular size. The $\Delta 2\text{INT}^*$ values contribute slightly unfavourably to the overall stabilisation of the packed systems, suggesting that only minor conformational strains were imposed by the framework structure. Similar results are obtained by comparing the energies for ASKs in TCMOR and in MOR113, on one hand, and the energies for ASKs in TCMTW and in MTW141, on the other hand ($\Delta 1\text{NBO}^*$ and $\Delta 1\text{INT}^*$).

No true molecular diffusion process could be revealed by the produced trajectories. Very low and statistically meaningless ($D \sim 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, comparable to the standard errors) slopes are obtained from the plots versus time of the atom coordinates' mean square deviations (MSD). The visual inspection of the MD trajectories reveals highly localised ASK motions around their preferred sites. The MSD plots were recalculated after subjecting the final 64 ps of each MD trajectory to FFT filtering into eight adjacent frequency intervals. This allows to examine slow ASK tumbling movements and ring conformational transitions separately from relatively shorter period motions (really high frequency atomic motions cannot be revealed, due to the adopted data sampling of 1 ps). Moreover, all FFT filtered MSD values seem to reproduce two different patterns, approximately corresponding to frequencies higher and lower than 5 cm^{-1} . In order to allow easier comparisons, these values were, respectively, reported as sum1 and sum2 (Fig. 4).

The results reveal clear differences in the mobility of the ASKs. The ASKs are generally more free to move when packed in the pores of MOR rather than in MTW, and the mobility of ASK II is observed to be lower than for ASK I and ASK III in both frameworks. Similar results were obtained when the MD simulations were run in the TCMOR cell, representing the pure effect of restrained packing space experienced by five ASKs, with no interactions with the zeolite pore walls. These conclusions qualitatively correlate with the packing stability scale derived from the POT* data: the higher the stability, the lower the mobility. The tighter packing imposed to nine ASKs by the TCMTW cell produces a similar order of increasing mobility, but with the value for ASK III being the lowest. Moreover, the steric hindrance caused by the zeolite pores is clearly evidenced by the comparison with the calculated mobility of a single ASK molecule in a large empty cell. In that case, the calculated mobility increases with the ASK bulkiness.

Corresponding effects were evidenced in the ^{13}C MAS NMR spectra [4], generally characterised by broad peaks of the ASK/zeolite samples (especially for ASK II) compared to the liquid phase ASKs, and by larger linewidths for ASKs in MTW with respect to MOR. Such linewidth broadening can be attributed to higher conformational constraints experienced by the ASKs and similar conclusions apply to the MSD results, even if the data were collected on a shorter timescale (100 ps) than what is accessible to the NMR experiments.

4. Conclusions

Molecular simulations were applied with the purpose of rationalising the shape and energy requirements that can drive the zeolite synthesis in the presence of SDA molecules. In a previous work [4] the SDA compatibility with the framework was correlated with the normalised binding energy (BE*) calculated by Monte Carlo docking and energy minimisation of a single ASK molecule. However, the extremely low selectivity of this class of compounds led to the crystallisation of several known zeolite structures and of the new ERS-10 phase.

In this study, the feasible ASK packing density in different zeolite pore systems was tested by MCP and

found reasonably consistent with the experimental determination of occupancy, in spite of the fact that the effect of solvent was not taken into account. The analysis of the energy contributions calculated along the MD simulations allowed to point out subtle differences in the relative stabilisation of the experimentally determined ASK packing in the framework of MOR and of MTW. A correlation between the calculated MSDs (at 300 K and on the timescale of 100 ps) in the zeolite pores and the ^{13}C MAS NMR linewidths helped the interpretation of different conformational constraints experienced by the ASKs in the two zeolite pores.

The available simulation results support the experimental evidence that the studied ASKs are well suited as SDAs in the hydrothermal synthesis of zeolites. In spite of the calculated and measured differences in the interaction energies and the mobility properties of the ASK/zeolite packing configurations, quite similar spatial and geometric requirements along the ring size

expanding series ASK I, II, III could be invoked to explain their rather low selectivity as SDAs of a specific zeolite framework.

References

- [1] R. Szostak, *Molecular Sieves. Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, 1989.
- [2] H. Gies, B. Marler, *Zeolites* 12 (1992) 42.
- [3] C. Carluccio, R. Millini, G. Bellussi, *Eur. Patent* 796,821 (1997).
- [4] R. Millini, L. Carluccio, F. Frigerio, G. Bellussi, W.O. Parker Jr., *Microporous Mesoporous Mater.* 24 (1998) 199.
- [5] D.W. Lewis, C.M. Freeman, C.R.A. Catlow, *J. Phys. Chem.* 99 (1995) 11194.
- [6] C.A. Fyfe, H. Gies, G.T. Kokotailo, B. Marler, D.E. Cox, *J. Phys. Chem.* 94 (1990) 3718.
- [7] A. Alberti, P. Davoli, G. Vezzalini, *Z. Kristallogr.* 175 (1986) 249.
- [8] *InsightII, Catalysis 4.0.0 and Discover 3.0 User Guides*, Molecular Simulations Inc., San Diego, USA, 1996.
- [9] J.-R. Hill, J. Sauer, *J. Phys. Chem.* 98 (1994) 1238.