

Enantioseparation in achiral zeolites: Effect of zeolite topology in relation to molecular properties of adsorbate molecules

1.- Purpose of the visit

During my previous visit to the host group, we studied, using molecular simulation, the chiral behavior that MFI type-zeolites (zeolites formed by zig-zag intersecting channels) exhibit when silicon atoms are exchanged by aluminum atoms. We used lactic acid enantiomers as adsorbate molecules. We also incorporated two novel Monte Carlo moves developed by the host group, into our computer code which proved enormous improvements for the statistical accuracy.

The purpose of my current visit to the Katholieke Universiteit Leuven is to study similar structures to MFI, like MEL, characterized by intersecting channels. In addition, we will focus on analyzing the chirality behavior in structures with very different topology such as FER and TON, characterized by longitudinal non-intersecting channels, and structures with large channels connected by windows, such as the FAU or LTA type-zeolites. At the other side, we plan to analyze how these different zeolite topologies link with the characteristic properties of the adsorbing molecule.

2.- Description of the work carried out during the visit

During my stay at the K.U. Leuven we work on the following aspects

1) We continued the work started during my last visit to the host group. This work consists on the analysis of the behavior of different mixtures with both enantiomers (R and S) of lactic acid (LAC) on MFI type zeolite. We also studied the separation of both enantiomers by substitution of some silicon atoms from the framework by aluminum atoms, and adding non-framework cations (calcium or sodium) to make zero the net charge of the systems.

2) The second idea was to analyze the behaviour of LAC on other zeolitic structures with different topologies. We focused on the influence that different topologies exert on the enantioseparation of LAC molecules. Due to the high computational requirements when one works with complex molecules such LAC, we analyzed first the smallest and simplest chiral molecule (CHCIFBr). In this section, the first step was to find in the literature, available models for a good definition of the molecule, and also a good force field to define properly the interactions between the molecules and the different structures under study. The second step was to compute the adsorption isotherms of mixtures formed by R- and S- CHCIFBr enantiomers in MEL, MFI, FER, TON, FAU, and LTA structures. To increase their separation capacities, we created different frameworks exchanging some atoms of silicon by aluminium, at different T-Site positions.

We created the following frameworks:

-MFI zeolite type pure silica, and this with 8 silicon atoms exchanged by aluminium atoms in T-Site positions 1, 2, 3, 4, 5, 6, 8, and 11. Positions 7, 9, 10, and 12 were not study, because they don't obey the Lowenstein's rule. To make zero the net charge of the systems we introduced 32 atoms of calcium.

-MEL zeolite type pure silica, this with 16 aluminium atoms in T-Site 2, and 8 aluminium atoms in T-Sites 6. Positions 1, 3, 4, 5, and 7 were not studied because they don't obey the Lowenstein's rule. To make zero the net charge of the systems with aluminium on it, we add 64 and 32 atoms of calcium respectively.

-FAU zeolite type pure silica, and with 96 silicon atoms exchanged by aluminium atoms in the T-Site position 2. Position 1 was not study, because it doesn't reproduce the Lowenstein's rule. To make zero the net charge of the systems we introduced 48 atoms of calcium.

-LTA zeolite type pure silica, and with 96 silicon atoms exchanged by aluminium in T-Site positions 1 and 2. To make zero the net charge of the system we introduced 48 calcium's atoms.

-TON zeolite type pure silica, and with 4 silicium changed by aluminium in T-Site positions 1 and 2. Structures with aluminium at T-Sites 3 and 4 don't obey the Lowenstein's rule, and we didn't study them. To make zero the net charge of the systems we introduced 40 atoms of calcium.

-FER zeolite type pure silica, and with 4 silicium changed by aluminium in T-Site positions 1, and 24 atoms of calcium to make zero the net charge of the system. Those with aluminium at T-Sites positions 2, 3, and 4 didn't obey the Lowenstein's rule.

Finally we analyzed the enantioselectivity behaviour of all the frameworks and mixtures under study.

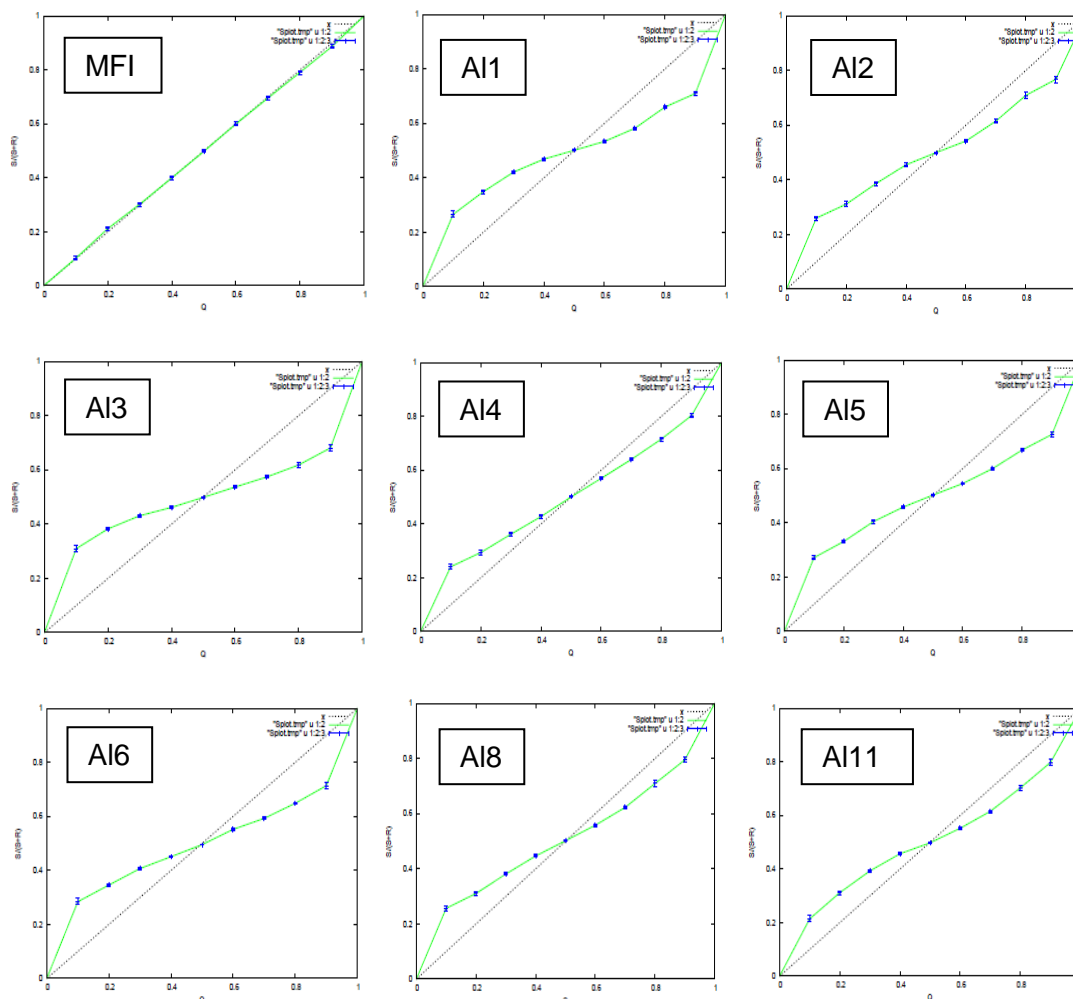
3.- Description of the main results obtained

After my first visit to the host group, we demonstrated that structures with non-framework calcium as cations, show more enantioselectivity that the ones with sodium. Therefore we focus our effort on them.

It is important to highlight that we had to add some improvements into our code to obtain the simulation data in a faster an efficient way. The validation of these improvements of the code took an important part of my research time. In addition, the simulations that we are performing involve very complex systems, with Coulombic and van der Waals interactions between hundred of atoms. The simulations are not completely finished yet, but I can present some preliminary results. To analyze the type of adsorption (homoselective or heteroselective), and the enantioselectivity on each system, we use the program developed by Dr. Titus van Erp.

1) Lactic Acid results:

As is possible to observe at the graphs below, MFI pure silica zeolite type doesn't present any capacity of separation of the enantiomers from LAC. By other way, the presence of aluminums and calcium in the structure increase this capacity of enantioseparation on the resulting frameworks. Different aluminum distribution, induce different enantioseparation behavior.



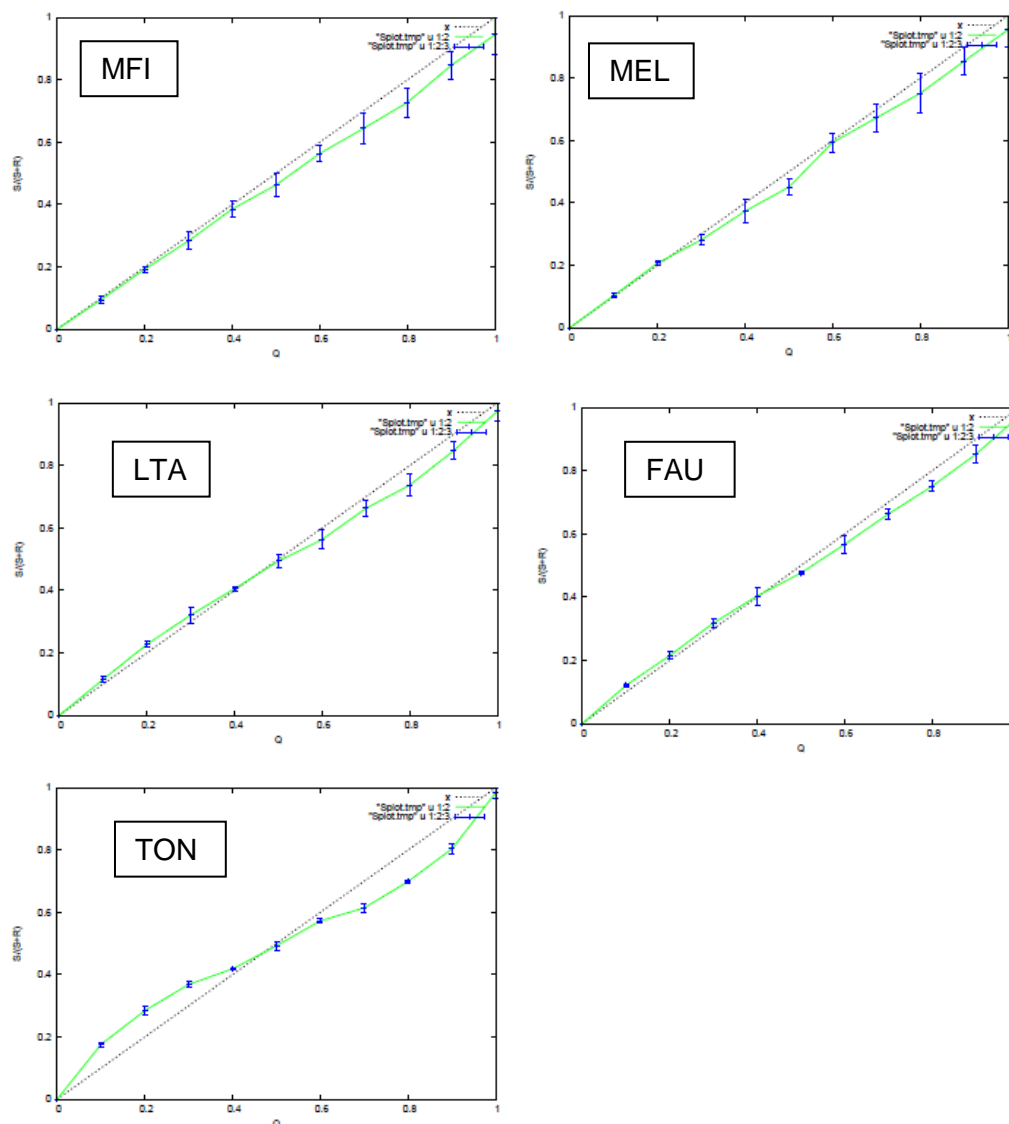
2) CHCIFBr results:

In this section the simulations are still running, so we only can show some preliminary results of the original structures under study, comparing frameworks with similar characteristics.

As mentioned above these results are preliminary, even so we can see that structures with similar characteristics have similar behavior:

- MFI and MEL zeolite types, characterized by longitudinal intersected channels, don't show any enantioseparation capacity.
- LTA and FAU structures, both characterized by the presence of aluminium atoms at T-Site position 2, and with large channels connected by windows, present a small capacity of enantioseparation.
- TON and FER, frameworks with longitudinal non-intersecting channels, surprising present a clear capacity for separation of chiral enantiomers. (Results from FER not available yet)

We are also working on the frameworks with aluminium at different T-Sites position, but still don't have reasonable results.



4.- Future collaboration with host institution

After my second visit at the K.U. Leuven, I plan to continue this work with Dr. Titus van Erp. We are also thinking on extending our collaboration to new projects, in fact we already have a new collaboration with an experimental group from the host institution with a similar goal than our for LAC, but using cyclic molecules. On the other hand the possibility to perform similar studies with other chiral molecules such as terpenes and geraniols is still open.

5.- Projected publications/articles resulting or to result from your grant

We established a significant progress in our simulation approach to treat the adsorption of polar molecules. Previous project between the host and our institution aimed at the adsorption of apolar molecules (chiral alkanes) which lead to publications in high impact journals (eg. *Angewandte*). During my first weeks in Leuven we found unexpected obstacles related to the polarity of LAC which prohibited an efficient sampling of our system. The previously applied protocols did not given proper ergodic behavior, the stronger interaction between the cations and LAC, compared to cations-alkane interactions, created permanent trapped states at energetically unfavorable conditions. We have invested considerable time to improve the efficiency using an additional set of MC moves. It is only very recent that we found satisfactorily parameters for the MC sampling. On the other hand, we hope and expect that the new sampling protocol will be effective for many other polar molecules that are now under investigation. Therefore, my stay in Leuven was very usefull and will probably initiate not only publications on this specific project (adsorption of LAC), but will prove to be fundamental for the adsorption of polar molecules in general. We will publish on these results once we have sufficient data.