SCREW DISLOCATIONS IN ZEOLITE A: A MOLECULAR HELTER SKELTER

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ABSTRACT

We have recently developed a new computational approach that allows us to predict the structure of dislocations in rather complex materials. This method was used to examine screw dislocations in the <100> direction in zeolite A, as recently seen on the {100} surface by AFM by Sacco and co-workers. Our predictions suggest that presence of a screw dislocation produces a new type of channel that has a larger average width than that of the perfect channel and may possess enhanced reactivity. More interesting still is that the channel has a handedness and is therefore capable of displaying enantioselectivity.

BACKGROUND

Dislocations are very important defects that provide edges on surfaces that are very favourable sites for crystal growth. Building units can adhere to the dislocation edge strongly because there are at least two points of contact in contrast with adhering to a pure surface where, attachment directly on the terrace is via one point of contact only. Growth spirals, caused by growth at dislocation source edges, have been observed on zeolite A and heulandite, and it is difficult to imagine that they are not present in many zeolitic materials prepared at moderate temperatures. Despite their obvious importance of line defects in the context of crystal growth, it is of great importance to learn how their structure differs from that of the perfect structure.

METHOD

Building upon work on simple oxides the early 1970's and more recently by Watson *et al.* in the 1990's, we have used a technique that combines a discrete atomistic model of the dislocation core with a description of the infinite crystal as an anisotropic linear elastic continuum. The construction of the simulation cell is cylindrical or puck-like; the inner core region, which is relaxed explicitly using a classical interatomic potential scheme, is embedded within an outer, fixed, region. Prior to relaxation the dislocation is introduced within the cell using the appropriate solution for the dislocation displacement field in an anisotropic elastic body with elastic constants calculated from the classical potential model. We considered two Burger's vectors, one with magnitude _**a**, where **a** is the lattice parameter of LTA, and 1**a**. The core strain is very long-ranged and therefore large puck diameters are necessary to converge the energy. In this work, we considered up to a 250Å diameter cell, containing up to 250,000 sites. For a system containing so many atoms it is necessary to treat the interactions between atoms in a special way. The puck is periodic in one direction (parallel to the dislocation) and a special summation technique due to Wolf *et al* is used to achieve the spatial decomposition necessary to calculate the long-ranged Coulomb forces within the disc.

RESULTS

The initial energy of the screw dislocation with two distinct Burgers vectors showed that the _**a** dislocation was very much more favourable than the 1**a** case. The _**a** case was fully relaxed and the accessible volume plotted shown in figure 1. The central part of the simulation 'cell' has been removed and a section removed to reveal the channel structure within the dislocation. The central channel is highlighted in black and shows the helical structure of the core, which has approximately constant diameter, perpendicular to the [100] axis. The helical channel contrasts with the neighbouring channels (grey), which shows large alpha cages connected by narrow eight rings. Perpendicular to the dislocation, the eight-ring channels are distorted into elliptical shapes, enhancing shape selectivity of anisotropic molecules. A further interesting feature is that the dislocation breaks the channel structure parallel to [100]; in the undefective material, the channel network is an uninterrupted 3D network but in this system, in traversing the core perpendicular to the dislocation, a sorbate must be filtered into another channel via the core, translating up or down by ~_**a**. These results indicate that regions of the zeolite containing dislocations will have special transport and uptake properties that should be considered when interpreting data. Finally, the presence of chiral channels within the zeolite opens up the possibility of exploiting materials such as zeolite A for enantiomer filtering.

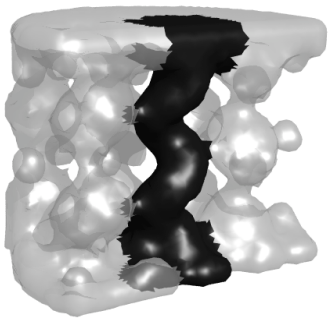

Figure 1: Screw dislocation in zeolite A

Keywords: Zeolite A, Screw Dislocation, Growth Spiral, Computer Simulation