Journal of Membrane Science 367 (2011) 63–70

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Enantioselective adsorption and diffusion of S-/R-glycidol in homochiral zeolites: A molecular simulation study

Liling Zhang, Jianwen Jiang*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Eng. Drive 4, Singapore 117576, Singapore

ARTICLE INFO

Article history:
Received 25 February 2010
Received in revised form 7 September 2010
Accepted 20 October 2010
Available online 27 October 2010

Keywords:
Enantiomers
Adsorption
Diffusion
Glycidol
Homochiral zeolites

ABSTRACT

As the first example of enantiopure homochiral zeolites, silicogermanates SU-32 can be synthesized in right- (SU-32a) or left-handed (SU-32b). These rare chiral zeolites provide beautiful benchmark structures to examine the microscopic properties of chiral molecules in the helical channels with only a single handedness. We report a molecular simulation study to investigate the enantioselective adsorption and diffusion of S-/R-glycidol enantiomers in SU-32a and SU-32b. S-glycidol is found to interact with SU-32a more strongly than R-glycidol and preferentially adsorbed in SU-32a, and the opposite is observed in SU-32b. The enantiomeric excess of S-/R-glycidol racemic mixture in SU-32a and SU-32b is up to 25% and slightly decreases with increasing temperature. For pure enantiomers, S-glycidol diffuses faster in SU-32a and slower in SU-32b, whereas the reverse is true for R-glycidol. The free energy analysis suggests that S-glycidol encounters a lower barrier to diffuse in SU-32a but a higher one in SU-32b. For S-/R-glycidol racemic mixture, the diffusion difference between two enantiomers becomes negligible as loading increases. This study reveals that enantiopure SU-32a and SU-32b have distinct enantioselectivity for glycidol enantiomers, particularly the selective adsorption, and might be useful for chiral separation.

1. Introduction

As a unique characteristic of Mother Nature, living organisms exhibit significantly different biological responses to chiral enantiomers. One enantiomer may have the desired pharmacological activity, while the other is usually inactive or toxic [1]. The production of enantiopure compounds is indispensable for pharmaceutical, food, agricultural and biotechnological industries. The considerable demand has spurred high-performance separation of chiral molecules. Currently, a number of techniques such as crystallization, kinetic resolution, chromatography, and membrane separation are used in laboratory or commercially [2–8]. The mechanism in chromatography and membrane-based chiral separation is recognized as the different affinities of enantiomers with chiral selector. Therefore, the judicious selection of a well-suited chiral selector is crucial to enantioseparation.

Chiral selectors are usually produced by two approaches. One is through direct synthesis from chiral molecules, e.g., cyclodextrins, crown ethers, proteins, DNA, and antibodies. Some of these materials, however, show poor enantioselectivity or low tolerance in harsh operation conditions. The other is to incorporate chiral molecules onto achiral supports such as silicas, nanotubes, metal surfaces, and membranes. Both approaches require the chiral molecules to possess enantioselective capability. As demonstrated experimentally, silica nanotubes grafted with an antibody onto the inner walls exhibit selective transport for enantiomers [9]. Chiral separation was also observed on chiral surfaces [10–13] and cellulose [14,15], and the selectivity was found to strongly depend on the interactions between enantiomers and asymmetric sites.

With the increasing demand of emerging chiral drugs and chemicals, there has been ever-growing interest in the development of new chiral selectors to achieve efficient enantioseparation. A number of porous materials exhibit chirality, such as silicas [16], zeolites [17], and metal-organic frameworks (MOFs) [18]. Intriguingly, they are constructed from achiral molecules, but assembled into left-handed or right-handed structures. These chiral materials have inherently chiral chains, ribbons, channels or networks, and are thus potentially useful for enantioseparation. For example, a chiral mesoporous silica was synthesized with surfactant as template and found to have enantioselective separation capability [19]. Several homochiral MOFs with a single chirality in their frameworks were reported and examined for enantioseparation [20–25]. Adsorption in homochiral MOFs from molecular simulations suggested that the collective effects of multiple chiral selectors play a crucial role in enantioselective adsorption [26,27].

Zeolites are chemically stable and commonly used in separation and catalysis; in this regard, they have been profoundly embraced as key functional materials in chemical industry. Chiral zeolites

* Corresponding author. Tel.: +65 65165083; fax: +65 67791936.
E-mail address: chejj@nus.edu.sg (J. Jiang).

0376-7388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2010.10.038

are a versatile addition to this arsenal [28] as they combine both shape and enantioselectivity, which are desirable for asymmetric catalysis and chiral separation. From molecular simulations, the adsorption of chiral molecules in heterochiral UCSB-7K and homochiral zeolite beta polymorph A (BEA) was investigated with the enantiomeric excess up to 40–70% in UCSB-7K and 10% in BEA [29]. It is noteworthy that zeolite BEA is a hypothetical structure and has yet been synthesized. This is because the synthesis of chiral zeolites remains a significant challenge. Currently, only three zeolitic frameworks exhibit chirality among 179 reported zeolites [30]. Zeolite beta is one of the most popular chiral zeotypes and consists of three-dimensional 12-ring channels interconnected in either left- or right-handed. Nevertheless, zeolite beta co-crystallizes in three polymorphs (A–C) and it is extremely difficult to obtain the enantiopure form. Zeolites are typically synthesized in the presence of surfactant templates, which are removed through calcinations at high temperatures. To synthesize chiral zeolites, chiral surfactants are used for the assembly of silicates into chiral structures. Unfortunately, the chiral structures are destroyed by calcinations and remain as either achiral or racemic mixtures.

Recently, enantiopure chiral silicogermanates SU-32 were synthesized [30]. They exhibit intrinsic chirality, i.e., the frameworks, channels and cavities all have a handedness. SU-32 are thermally stable up to 400 °C and possess helical channels of approximately 5.5 Å × 5.0 Å. Unlike zeolite beta and other chiral zeolites, enantiomorphic pure SU-32 can be crystallized in either right- (SU-32a) or left-handed (SU-32b). Therefore, these rare chiral zeolites provide beautiful benchmark structures to study the microscopic properties of chiral molecules in the helical channels with only a single handedness. The insights gained could be useful for the separation of chiral molecules and to facilitate the further development of chiral porous materials.

In this work, we investigate the enantioselective adsorption and diffusion of S- and R-glycidol enantiomers in SU-32a and SU-32b using molecular simulations. With the continuous growth of computational power, simulations at a molecular scale can provide microscopic pictures that are otherwise experimentally inaccessible or difficult to obtain, and thus complement and guide experimental studies. In Section 2, the models for SU-32a/SU-32b and glycidol are briefly described along with the force field used. The methods are introduced in Section 3, including Monte Carlo (MC) simulation for adsorption and molecular dynamics (MD) simulation for diffusion. In Section 4, we first present the interactions of single S- and R-glycidol with SU-32a and SU-32b at 300 K, and then the adsorption isotherms and enantiomeric excesses of S-/R-glycidol racemic mixture at 250, 300, and 350 K. Next, the diffusivities and activation energies of single S- and R-glycidol in SU-32a and SU-32b are reported. The diffusion of pure S- or R-glycidol is further examined at finite loadings; the density and free energy profiles are calculated along the channel axis to estiamte diffusion barrier. Finally, the diffusion of S-/R-glycidol racemic mixture is examined at different loadings in SU-32a and SU-32b. The concluding remarks are summarized in Section 5.

2. Models

Silicogermanate SU-32 are assembled from building block TO_4 tetrahedra (T = Si or Ge) [30]. There exist two pure enantiomorphs, namely, right-handed SU-32a and left-handed SU-32b. The lattice constants are $a = b = 12.2635$ Å and $c = 30.2527$ Å in SU-32a, and $a = b = 12.2476$ Å and $c = 30.1430$ Å in SU-32b. By symmetry, two enantiomorphs should in principle have identical lattice parameters. The slightly different parameters measured in SU-32a and SU-32b might attribute to the experimental uncertainty in X-ray diffraction. In this work, pure-silica SU-32a and SU-32b were considered and their crystal structures were constructed on the basis of the experimental crystallographic data [30]. As demonstrated in experiment, the organic ligands in SU-32 could be removed and the geometry-optimized structures of pure-silica SU-32 equivalents remained largely similar to silicogermanates. Building layers with 4-, 5-, and 12-rings exist in SU-32 and the adjacent layers are related to one another by a 60° rotation. The 12-rings from adjacent layers are rotated and shifted from each other, thus the 12-ring channels are blocked by the 10-ring windows. The helical channels running along the Z-axis are built from $4^6 5^8 8^2 10^2$ cages connected via the 10-ring windows. The helical channels at different heights are intersected by the 8-ring channels [30].

Fig. 1 shows the morphologies and sizes of the helical channels in SU-32a and SU-32b along the Z-axis. It can be seen that SU-32a has right-handed channels, while SU-32b has left-handed. Each structure is shown with 18 ($3 \times 3 \times 2$) unit cells and there are nine paralleled channels along the Z-axis. The sizes were calculated using HOLE program [31] and range from 2.4 to 2.8 Å in radius. The green color denotes narrow window with a radius of 2.4–2.6 Å, while the blue color denotes cage with a radius of 2.6–2.8 Å. There are six periodic cages-and-windows along the Z-axis in a unit cell and each cage is connected to its neighbors by a 60° rotation, leading to the helical channel. Fig. 2 shows the atomic structures and charges of S- and R-glycidol. Widely used as an intermediate in organic synthesis, glycidol is a chiral molecule containing epoxide. The hydroxyl group experiences a strong interaction in the helical channels of SU-32, which could lead to enantioselectivity.

3. Methods

To estimate the interaction energies of S- and R-glycidol with SU-32a and SU-32b at infinite dilution, Monte Carlo simulations were carried out in a canonical ensemble (NVT) using Materials Studio [32]. A single glycidol molecule was used and temperature was at 300 K. The simulation box contained ($3 \times 3 \times 1$) unit cells with nine channels along the Z-axis and the periodic boundary conditions were exerted in three dimensions. The zeolitic framework atoms were kept rigid during simulation. Both zeolite and glycidol atoms were modeled by the polymer-consistent force field (PCFF) [33,34]. In the PCFF, the bonded interactions include bond stretching, angle bending and dihedral torsion; while the nonbonded interactions consist of 9–6 dispersive and Coulombic potentials. The dispersive interactions were evaluated by atom-based method with a spherical cutoff of 12 Å and a cubic splice width of 1.0 Å. The Coulombic interactions were estimated by the Ewald sum with an accuracy of 10^{-5} kcal/mol. To accelerate configuration sampling, the configurational-bias technique was used. Three types of trial moves were conducted randomly in the NVT simulations, including translation with a maximum step of 1.0 Å, twist and rotation each with a maximum angle of 5°. For the adsorption of S-/R-glycidol racemic mixture, grand canonical Monte Carlo (GCMC) simulations were performed at 250, 300 and 350 K, respectively. In addition to the three types of trial moves mentioned above, deletion and insertion were also conduced with equal probability. The number of trial moves in a typical GCMC simulation was 2×10^7, in which the first half were used for equilibration and the second half for ensemble averages.

MD simulations were conducted to examine the diffusion of glycidol enantiomers in SU-32a and SU-32b using DL_POLY [35]. The structure files created by Materials Studio were converted to DL_POLY by an in-house code. In such a way, the computational speed was accelerated by one to two orders of magnitude. More specifically, three sets of MD simulations were run. First, the diffusivities of single S- and R-glycidol (at infinite dilution) were calcualted at various temperatures, from which the activation ener-