

Phase selectivity in the syntheses of cage-based zeolite structures: An investigation of thermodynamic interactions between zeolite hosts and structure directing agents by molecular modeling

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

In this investigation we use molecular modeling to determine the van der Waals stabilizations of piperidinium derivatives and polycyclic quaternary ammonium compounds in zeolite frameworks with cage-based structures: **NON**, **SGT**, **DDR**, **AEI**, **CHA**, **ITE**, and **STF**. This effort follows earlier work by our group that studied the phase selectivities of these structure-directing agents (SDAs) under different conditions of synthesis [Y. Nakagawa, G.S. Lee, T.V. Harris, L.T. Yuen, S.I. Zones, *Micropor. Mesopor. Mater.* 22 (1998) 69–85; P. Wagner, Y. Nakagawa, G.S. Lee, M.E. Davis, S. Elomari, R.C. Medrud, S.I. Zones, *J. Am. Chem. Soc.* 122 (2000) 263–273; G.S. Lee, S.I. Zones, *J. Solid State Chem.* 167 (2002) 289–298]. The stabilization energies are found to be a good indicator of selectivity for phases that often crystallize within the same inorganic conditions (e.g., **AEI** and **CHA**, **ITE** and **STF**). The calculated stabilization energies are especially good indicators of phase selectivity for the large polycyclic molecules. Although the predictions for the piperidinium derivatives are not as successful at distinguishing selectivity for **ITE/STF** pair, we again find that the larger molecules among this group are accurately predicted. We suggest that this may be due either to a greater number of configurations available in the **ITE** cage or to the greater rotational freedom permitted for the smaller molecules in the round **ITE** cage. We next compare the differences in stabilizations of the different SDA/framework pairs with the differences in their respective framework energies, which have been approximated from empirical relations derived from earlier calorimetry experiments by Piccione et al. In general, these differences are found to be of similar magnitude for different phases that crystallize with the same SDA. Finally, we discuss the effects that siloxy/silanol defects may have on the frequently observed trends in the framework density for series of phases that are crystallized with the same SDA.

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1. Introduction

In this presentation we will focus on some elements of zeolite phase selectivity when products are formed in the presence of organo-cations. The topic of phase selectivity and crystal growth was one of great interest to Prof. Kokotailo. Indeed, during visits to our laboratory to see his good friend, the late Robert van Nordstrand, our group was for-

tunate to be able to listen to their discussions concerning zeolite crystal growth and polymorphism. Both men were leaders in the field in understanding zeolite structures, and each had a keen interest in the details of their formation. The present contribution represents some of the advances made since those days. This has been made possible by a larger database of zeolite products and examples of their formation from an array of organo-cations, as well as by advances in computational chemistry.

In previous publications our research group has reported the use of polycyclic quaternary ammonium

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compounds and piperidine derivatives as structure directing agents (SDAs) for various zeolite phases [1–3]. Tables 1 and 2 summarize the synthesis results obtained for these SDA molecules in gels with different starting silica/alumina ratios (SAR) and in gels with silica/boron oxide ratio = 40. The details of these syntheses may be found in Refs. [1–3].

We observed that many of these molecules are particularly selective for zeolites with large cage structures. These zeolite phases include SSZ-13 (**CHA**, FD = 15.4 tetrahedral atom/1000 Å³), SSZ-39 (**AEI**, FD = 15.0), SSZ-36 (**ITE/RTH** intergrowth, FD = 16.3, 16.6), SSZ-35 (**STF**, FD = 17.3), SSZ-44 (**SFF**, FD = 17.2), Sigma-2 (**SGT**, FD = 17.8), SSZ-28 (**DDR**, FD = 17.6), and nonasil (**NON**, FD = 19.3). Here we have enumerated the three-letter IZA code [4] along with the tetrahedral (T) atom framework density (FD) determined from crystallographic reports of the most siliceous form of each zeolite. The FDs will be relevant in our subsequent discussions of phase selectivity. For simplicity, we refer to each zeolite phase by its three-letter code. Fig. 1 shows the large cage structures present in each of the zeolite topologies that we discuss in this work. Note that the cage structures are drawn to scale to allow a direct comparison of the dimensions of each cage. In some cases the cages are presented at different angles to highlight the relative dimensions within each cage. For example, one view of the **NON** cage suggests that it is as voluminous as the **CHA** and **AEI** cages. However, 90° rotations of the **NON** cage show that it is actually quite narrow in two of its dimensions. In contrast, the **SGT** and **ITE** cages have similar dimensions along each of their major axes.

The **CHA** and **AEI** frameworks possess similar FD, and each structure possesses 12 T atom/cage. This is not surprising when one considers that both structures can be built from layers of interconnected double six-rings (D6Rs). In **AEI**, the neighboring layers are related by mirror planes, and in **CHA** these layers are related by translational symmetry. The **AEI** and **CHA** cages enclose the same volumes, but their shapes are dramatically different. The **CHA** cage is shaped like a cylinder, whereas the **AEI** cage is shaped like a pear. The length of each cage is about the same, but the cage width varies in **AEI** while it remains fairly uniform in **CHA**. These differences in shape will be especially relevant in our discussion of phase selectivity.

The **ITE/RTH** (16 T atom/cage) and **STF/SFF** (16 T atom/cage) pairs possess a symmetry relationship similar to the **AEI/CHA** pair. **ITE** possesses layers related by mirror planes [5,6], whereas those same layers are related by inversion centers in **RTH** [7]. However, in this case there are only minor changes in the relative dimensions of the two cages. In fact, Fig. 1 shows that both cages possess spheroidal shapes, and the key differences in shape can be clearly discerned only along a single projection. Many of the SDA we present in this study produce **ITE/RTH** intergrowths (SSZ-36, Ref. [2]), which may be an indication of the similar framework/SDA interactions that exist for the two frameworks. Likewise, the **STF** and **SFF** cages possess similar dimensions and the subtle differences in shape are

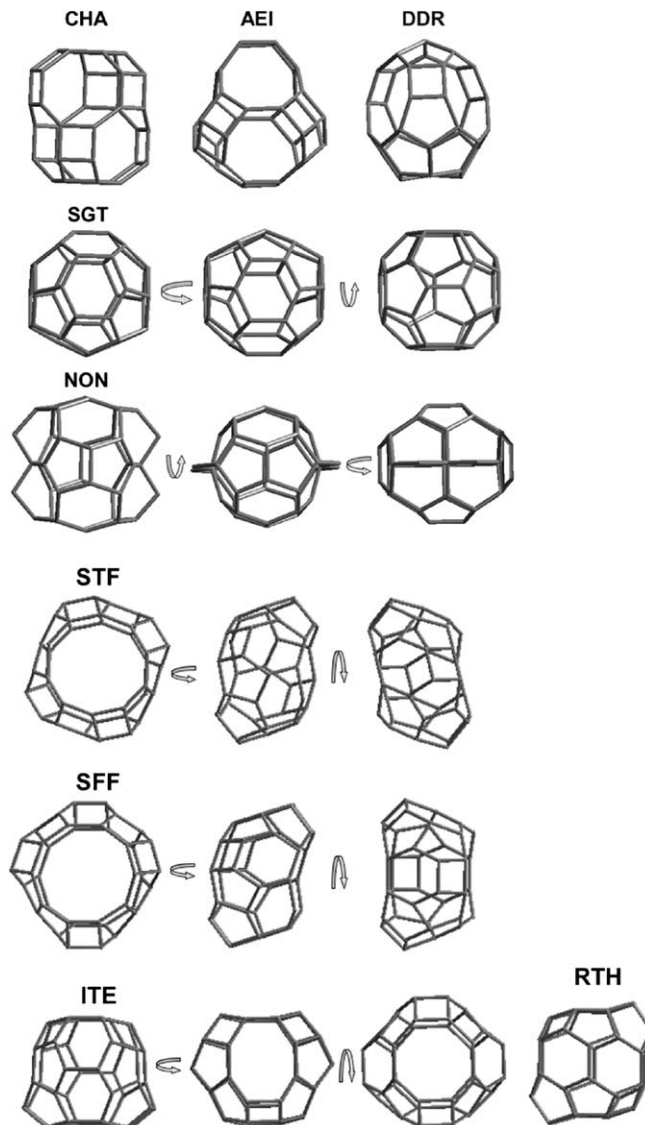


Fig. 1. The largest cage features observed in the phases discussed in this study.

only readily apparent along a single projection [8]. The volumes of the **STF/SFF** cages are similar to the **ITE/RTH** cages, but the cages are more flat along one dimension and wider along the other two. Surprisingly, although the cages have similar shapes and their SDA/framework interactions are usually calculated to be about the same, **STF/SFF** intergrowths are rarely observed. In fact, only one SDA molecule (E) yields an **SFF** structure, and the frequently observed SSZ-35 (**STF**) is usually prepared with few or no stacking faults. However, Morris et al. have recently reported the crystallization of **STF/SFF** intergrowths in syntheses performed in fluoride media using molecule E, which is highly selective for **SFF** phases in hydroxide gels. They found that the intergrowth character can be controlled by varying the SiO₂/H₂O ratios in these syntheses [9]. In our molecular modeling (work not presented), we have not found a significant difference in the stabilizations of this SDA within the **STF** and **SFF**

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