# Computational and Experimental Approach to the Role of Structure-Directing Agents in the Synthesis of Zeolites: The Case of Cyclohexyl Alkyl Pyrrolidinium Salts in the Synthesis of $\beta$ , EU-1, ZSM-11, and ZSM-12 Zeolites

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The role of structure-directing agents (SDA) in the synthesis of zeolites is investigated, and the structures obtained in the synthesis are rationalized in terms of the energetic stabilization between the SDA and the microporous zeolite structure. An explanation is provided for the synthesis outcome in terms of a balance between kinetic and thermodynamic factors throughout the nucleation and crystallization stages. The stability of  $\beta$ , EU-1, ZSM-11, and ZSM-12 zeolites is calculated over a wide range of Si/Al ratios when cyclohexyl alkyl pyrrolidinium salts are used as the SDA. The role of the SDA allows us to explain the final stability and the Si/Al range in which each structure can be synthesized. The stabilization of intermediate species during the nucleation is proposed to orient the final result of the synthesis. A simple kinetic model is proposed to explain the synthesis process.

# 1. Introduction

The ability of certain organic and inorganic species to direct the synthesis of crystalline aluminosilicates toward a particular structure is determined by kinetic and thermodynamic factors, the latter being determined by the stabilization gained by the system SDA-zeolite with respect to the separate components. The use of suitable organic SDA molecules in the synthesis allows us to select between possible phases with a priori similar thermodynamic stability<sup>1,2</sup> and allows us to make more energetically favorable the synthesis of a given structure. Framework inorganic cations can also have an influence in the first stages of the synthesis during the nucleation process by orienting the formation of Si-O-T (T = tetrahedral atom) oligomers toward certain secondary building units that influence the final crystallized structure(s).3-5 Other factors, such as OH/Si and TIV/TIII ratios, are also crucial in directing the synthesis toward a particular zeolite.

The organic can sometimes act as a pore-filling agent, and when this occurs, the structure-directing effect of the organic is limited. In other syntheses, an important interaction between the SDA and the framework occurs, and then the selectivity of the organic toward the formation of a given structure is higher than in the previous case. Finally, there are very few structures in which a full match between the organic and the inorganic counterpart exists and the SDA can be considered to be a template for that particular structure.<sup>6–11</sup> Quaternary ammonium salts have become widely used as SDAs because they allow strict control of the hydrophobic/hydrophilic properties by controlling the C/N<sup>+</sup> ratio of molecules within a large range of sizes and shapes.

Computational methods help us to understand better the physicochemical interactions between the SDA and the zeolite framework. Lewis et al.<sup>12</sup> have combined Monte Carlo and

energy minimization techniques to calculate the stability and location of tetraalkylammonium cations in ZSM-5, ZSM-11, and  $\beta$  zeolites and bis-quaternary amines in EU-1 and ZSM-23. Their results allow us to achieve a de novo synthesis by selecting the appropriate template for a particular structure. A similar technique was used to explain the influence of the SDA molecule and cobalt concentration in the competitive formation of Co-AlPO-5 and Co-AlPO-34 starting from similar synthesis gel compositions.<sup>13</sup> Monte Carlo docking algorithms based on a force field approach combined with crystallographic data have been used by Toby et al.<sup>14</sup> to study the effect of structuredirecting agents in the inhibition or formation of stacking faults in CIT-1. A number of other studies based on computer simulation of the rationalization of zeolite synthesis are available in the literature,<sup>15–18</sup> and they predict the stability of organic species occluded in microporous materials. Recent studies by Shantz et al.<sup>19–21</sup> explain how the distribution of framework aluminum in ZSM-12 can be controlled by the template location, and a similar effect has been observed in ZSM-18.22 The purpose of this work is to test two SDAs with related molecular structures and C/N<sup>+</sup> ratios that should behave similarly from the point of view of pH, solubility, and hydrophobicity. However, the geometrical differences in the two molecules should influence the energies of zeolite-SDA interactions and the stability of the pores and topologies formed. The experimental results obtained by using these SDA molecules in the synthesis of zeolites will be rationalized on the basis of molecular simulations.

### 2. Experimental Section

The SDAs were prepared by following a well-known methodology, namely, the reductive amination of carbonylic compounds.<sup>23</sup> In this case, the reaction proceeds via a condensation between an amine and a ketone at pH  $\leq$  8, thus forming an imine or enamine (depending on whether the amine is primary or secondary). Under these experimental conditions,

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SCHEME 1: Mechanism of the Reductive Amination Methodology



both the imine and enamine are reduced as imminium salts to form the new amines (Scheme 1) that are finally quaternized by reaction with an alkylhalide, namely, iodomethane or bromobutane, to yield to the quaternary tetraalkylammonium. The initial amine that was chosen was pyrrolidine, which had already been used in the form of the *N*,*N*-dimethyl-pyrrolidinium cation for the synthesis of other zeolites. This cation showed, under certain conditions, a low structure selectivity, and a wide mixture of medium- and large-pore zeolites as well as clathrasils was obtained. It was thought that when using the pyrrolidine in the reductive amination of cyclohexanone a series of larger molecules that could be transformed into quaternary ammonium salts would be of better selectivity and at the same time their use may avoid the formation of clathrasils. Scheme 2 shows the cations obtained and their corresponding C/N<sup>+</sup> ratios.

2.1. Synthesis of Structure-Directing Agents. Quaternary ammonium salts were prepared from a series of amines, synthesized by the reductive amination strategy mentioned above. The following procedure was generally used: 50 mL of 5 N HCl-methanol was added to a solution of 44.6 g (638 mmol) of pyrrolidine in 200 mL of methanol, followed by the addition of 10.0 g (102 mmol) of cyclohexanone and 5.1 g (81 mmol) of NaBH<sub>3</sub>CN. The resulting solution was stirred for 72 h and then concentrated, and 5 N HCl was added until pH < 2was reached. Then, the methanol was removed under vacuum at room temperature. The residue was washed and purified with two 200-mL portions of ether. The aqueous solution was brought to pH > 12 with KOH, saturated with NaCl, and extracted with three 100-mL portions of ether. The organic extract was dried (MgSO<sub>4</sub>) and evaporated in vacuum. The resulting tertiary amines were quaternized with different alkyl halides as follows: a 250-mL round-bottom flask was charged with 10.0 g (65.4 mmol) of the cyclohexylpyrrolidine amine and 100 mL of CHCl<sub>3</sub>. A solution of 126.7 mmol of alkyl iodide (methyl or butyl bromide) and 50 mL of CHCl3 was added dropwise. A white solid was formed almost immediately. The reaction was stirred at room temperature for 3 days. The solid was collected by filtration, washed exhaustively with ether, and dried.

**Characterization Data for Compound 1.** <sup>13</sup>C NMR (200 MHz; D<sub>2</sub>O): δ 81.75, 70.63, 58.5, 34.27, 31.89, 31.59, 27.91.





Anal. Calcd for C<sub>11</sub>H<sub>23</sub>NO: C, 44.7; H, 7.8; N, 4.75. Found: C, 43.5; H, 8.05; N, 4.83.

**Characterization Data for Compound 2.** <sup>13</sup>C NMR (200 MHz; D<sub>2</sub>O):  $\delta$  77.28, 66.83, 62.84, 33.68, 32.06, 31.58, 30.63, 15.48. Anal. Calcd for C<sub>14</sub>H<sub>28</sub>BrN (+2H<sub>2</sub>O): C, 51.54; H, 9.81; N, 4.30. Found: C, 51.51; H, 9.45; N, 4.23.

The above synthesized halide tetraalkylammonium salts were transformed to the corresponding hydroxide forms by anionic exchange using a DOWEX resin in a water solution. The degree of exchange always leaves the halide concentration below the detection limit of the corresponding selective electrode. Therefore, the total concentration of SDAOH was achieved by acid titration using phenolphthaleine as an indicator.

**2.2.** Synthesis of Zeolites. The influence of the different structure-directing agents on the synthesis of zeolites was tested in gels having the following general molar composition:  $SiO_2/xAl_2O_3/0.54SDA(OH)/0.54HF/7.25H_2O$ . SDA(OH) is the structure-directing agent employed in each synthesis. SiO<sub>2</sub> was incorporated into the synthesis gel as tetraethylortosilicate (TEOS from Aldrich), and  $Al_2O_3$ , as aluminum triisopropoxide (AIP from Aldrich Co.). The influence of the aluminum content in the synthesis gel was studied by varying *x* ratios between 0 and 0.0333.

In a typical synthesis, TEOS and AIP were added to a SDA-(OH) solution. The initial clear solution was vigorously stirred until the alcohols produced during the hydrolysis of TEOS and AIP were completely removed and the required water content was reached by slow evaporation at 25 °C. Then, a 50 wt % aqueous solution of HF was added to the above reaction mixture, resulting in the immediate formation of a very thick gel that was manually homogenized. The final gel was loaded in Teflonlined stainless steel autoclaves at different temperatures (135, 150, and 175 °C), and samples were withdrawn at different crystallization times. The resulting zeolitic materials were collected by filtration, exhaustively washed with distilled water and acetone, and finally dried at 100 °C overnight. The different zeolite phases formed during the crystallization process were identified by an X-ray diffraction technique. The different

**TABLE 1:** Synthesis Conditions and Detected Phases

SDA cation	Si/Al <sub>gel</sub>	temperature (°C)	time (days)	phase	sample
1	~	135	16 21	$\beta$ ZSM-12 + $\beta$	1 2
		150	4 10	$ZSM-12 + \beta$ ZSM-12	3 4
		175	4	ZSM-12	5
	50	135	17	EU-1	6
		150	14	EU-1	7
	25	175	16	ВО-1 В	0
	25	175	10	$\rho$	9
2	15	1/5	15	$\rho$ + laminar phase	10
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	150	14	$\beta$ + ZSM-11	11
		150	42	ZSM-11	12
		175	5 12	$\beta$ + ZSM-11 ZSM-11	13 14
	50	175	3	ZSM-11	15
	25	175	18	ZSM-11	16
	Normalised Intensity			Sample 14 Sample 6 Manufactorial Sample 4 Sample 1 Sample 1 Manufactorial Sample 1	

Figure 1. XRD patterns of some representative samples.

synthesis gel compositions and the zeolite phases observed in this work are listed in Table 1. Also, representative XRD patterns of the different phases that were detected are shown in Figure 1. XRD patterns were acquired using Cu K $\alpha$  radiation on a Phillips X'Pert MPD diffractometer equipped with a PW3050 goniometer using secondary monochromated Cu K $\alpha$  radiation and a step size and time per step of 0.02° and 2 s, respectively.

It was observed that the use of cation 1 in the synthesis of purely siliceous zeolites yields the formation of zeolite  $\beta$  when low crystallization temperatures or times are used (samples 1–3 in Table 1), whereas the ZSM-12 structure is the unique phase detected after crystallization at high temperatures or relatively long synthesis times (samples 4 and 5). Similar results were observed in the syntheses carried out in the presence of cation 2, but in this case, the end product was the ZSM-11 structure instead of the ZSM-12 zeolite. These results indicate that zeolite  $\beta$  seems to be a kinetic product rather than the thermodynamic solid using either cation 1 or 2. Therefore, most of the study presented here was performed at relatively high temperature (175 °C) and prolonged crystalization times.

It is well known that by introducing Al into the synthesis gels in the presence of cation 1 the SDA gives way to the formation of different phases of those obtained by the analogous purely siliceous ones. In fact, EU-1 was the unique phase detected when the Si/Al ratio of the synthesis was 50, and  $\beta$  becomes the most stable product by further increasing the Al content until the Si/Al ratio is 25. Finally, lamellar phases start to be formed in the synthesis gel of a Si/Al ratio of 15. This indicates that there is a clear directing effect toward more open structures as the Al content in the gel (and also in the final solids) increases. This result can be rationalized by considering that the amount of compensating positive charged cations occluded within the zeolitic micropores must increase as the aluminum content increases; therefore, more open structures, such as  $\beta$  or EU-1, will be favored.

#### **3.** Computational Methods

The calculations have been performed using lattice-energy minimization techniques and the GULP code.<sup>24</sup> The interatomic potentials used to model the interactions between the atoms in the zeolite structure included the following terms: Coulombic interaction, short-range pair potentials (described by a Buckingham function), and a three-body bond-bending term. The shell model was used to simulate the polarizability of the oxygen atoms. A cutoff distance of 12 Å was applied to the short-range interactions (Buckingham- and Lennard-Jones-type interactions, see eqs 3 and 6 below). The Ewald summation technique has been used for the summation of the long-range Coulombic interactions. The potentials used for the zeolite25,26 were parametrized to reproduce the structure of the  $\alpha$ -quartz and have been demonstrated to model a number of zeotype structures successfully.<sup>27-30</sup> The force field by Kiselev et al.<sup>31</sup> was selected for the intermolecular SDA-zeolite and SDA-SDA interactions, and the force field by Oie et al.32 was selected for intramolecular interactions between the atoms of the SDA. For the organic SDA, the charge distribution has been obtained by means of the quantum chemistry Hartree-Fock method by using a 6-31G\*\*<sup>33</sup> basis set, and the calculations have been performed by means of the NWCHEM package.<sup>34</sup> More details of the computational methods can be found elsewhere.<sup>35,36</sup> The total potential energy function and the respective terms are as follows:

$$V_{\text{total}} = V_{\text{zeo}} + V_{\text{SDA}} + V_{\text{SDA}-\text{SDA}} + V_{\text{zeo}-\text{SDA}}$$
(1)

$$V_{\text{zeo}} = V_{\text{Buckingham}} + V_{\text{Coulombic}} + V_{\text{three body}} + V_{\text{core-shell}}$$
(2)

$$V_{\text{SDA}} = V_{\text{two body}} + V_{\text{three body}} + V_{\text{four body}} + V_{\text{Coulombic}}$$
(3)

$$V_{\rm SDA-SDA} = V_{\rm Lennard-Jones} + V_{\rm Coulombic} \tag{4}$$

$$V_{\text{zeo-SDA}} = V_{\text{Lennard-Jones}} + V_{\text{Coulombic}}$$
(5)

$$V_{ij}(\text{Buckingham}) = A_{ij} \cdot \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C_{ij}}{r^6}$$
(6)

$$V_{ij}(\text{Coulombic}) = \frac{q_i \cdot q_j}{r_{ij}} \tag{7}$$

$$V_{ijk}(\text{three body}) = \frac{1}{2} k_{ijk} \cdot (\theta_{ijk} - \theta_{ijk}^{0})^{2}$$
  
with  $\theta = \text{O}-\text{T}-\text{O}$  (8)

$$V_{ij}(\text{core-shell}) = \frac{1}{2}k_{ij} \cdot (r_{ij} - r_{ij}^0)^2$$
(9)

$$V_{ij}(\text{two body}) = \frac{1}{2}k_{ij} \cdot (r_{ij} - r_{ij}^0)^2$$
(10)

$$V_{ijkl}(\text{four body}) = A_{ijkl} \cdot [1 + \cos(n \cdot \phi_{ijkl} - \delta_{ijkl})]$$
(11)

$$V_{ij}(\text{Lennard-Jones}) = \frac{B_{ij}}{r^{12}} - \frac{C_{ij}}{r^6}$$
(12)



**Figure 2.** Energy scheme (top) for the synthesis of two zeolite structures (Z) in the presence of a SDA starting from the same gel (G) and going through different nuclei (N). Path 1 requires less activation energy for the nucleation stage, and path 2 gives the most stable final structure. A mechanism (middle) in two stages is proposed with a reversible nucleation followed by the crystallization. Nuclei form (bottom) when silicoalumina oligomers surround the SDA, giving an aggregate resembling a significant part of a structure.

A final consideration regarding the methodology that was used concerns the possible presence of water in these systems and whether water should be included in the calculations. It is known that zeolites synthesized as high Si/Al ratio materials and in the presence of fluoride anions are obtained as nondefective materials and therefore are highly hydrophobic, this being the case for the syntheses reported here, which makes the influence of water unimportant.

Also, it is generally accepted that the synthesis of zeolites occurs through consecutives steps. The most important step consists of the organization of the hydrophobic organocation with silicate species in solution. This interaction proceeds via an overlap of the hydration spheres, and then there is a strong interaction between the hydrophobic organocation and the silicate oligomers. It has been proven that this second step leads to phase selectivity toward a precise zeolite structure, and the presence of water molecules does not seem to be of importance; in fact, it is thought that water is mostly excluded in the formation of these prenuclation composites. This concept is fulfilled by the empirical observation that the largest organocation is the most selective toward a single phase. In our calculations, we have tried to model these composites as the starting point during zeolite formation; therefore, water has not been included in our calculations.

## 4. Theory

Microporous materials provide a host-type environment for stabilizing charged molecular species occluded in their cavities. The stabilization of the "zeolite–guest" system with respect to the separate components, "zeolite + guest", is due to the interactions between the guest and the zeolite. The energy change in the synthesis process starts from the initial reactants (a silica–alumina gel plus the organic SDAs) and goes toward the final zeolite–SDA system.

**4.1. Kinetic and Thermodynamic Aspects during the Zeolite Synthesis.** The synthesis of zeolites may be seen (Figure 2) as a series of consecutive reactions that occur starting from the gel, and then silicoalumina oligomers start to form (prenucleation). Clusters of secondary building units or zeolite fragments of little significance then appear when small nuclei grow (nucleation), and this occurs around the SDA cations if they are present in the synthesis gel. Larger nuclei continue to grow and lead eventually to the final zeolite structure (crystallization). In a simplified treatment, we consider the nucleation and crystallization to be the two main steps (Figure 2). It is seen that there are two competitive consecutive reactions, each of them leading during the nucleation stage to the formation of a stable nucleus  $(N_1, N_2)$  that consists of the SDA cations

surrounded by a series of silica oligomers adopting a distribution resembling that of a significant zeolitic fragment. Two approximations to such possible nuclei, for the sake of visualization, are also depicted in Figure 2. The energy of such possible aggregates depends mainly on two energetic terms: the energy of the corresponding SDA conformation and the stabilization due to interactions between the SDA and the silicoalumina oligomers forming the nucleus. For a more detailed analysis of these two contributions and all of the other terms contributing to the total energy, see Appendix 1. The relative stability of the different nuclei (N1, N2) will give us an estimation of which zeolite is preferentially forming during the early stages of the synthesis. It is clear from our kinetic model that if N1 is formed preferentially then Z<sub>1</sub>-SDA will be the synthesis product, independently of whether it is more or less stable than Z<sub>2</sub>-SDA. The thermodynamic product  $(Z_2-SDA)$  in the case illustrated in Figure 2) will be the synthesis outcome when the activation energies are low enough to compete with parallel reactions. Increasing the temperature and time of the synthesis will favor the thermodynamic product. Although this is a simplified treatment and aspects such as, for example, the competitive reactions between nucleus formation and dissolution are more complex, the basic phenomena of the zeolite synthesis are undertaken by our model.

**4.2. Graphic Representation of Zeolite Stability at Different Al Contents.** Our approach aims to answer the question of which zeolite structure(s) is(are) thermodynamically favored from a given set of initial conditions.

Starting from the question of which zeolite(s) is(are) preferentially formed from a given set of initial conditions, the following equations can be written:

$$gel(m_1Si, n_1Al) + n_1SDA^+ + x_1SDA^0 \rightarrow zeo_1 - SDA \quad (13)$$
$$gel(m_2Si, n_2Al) + n_2SDA^+ + x_2SDA^0 \rightarrow zeo_2 - SDA$$

To calculate the zeolite-SDA energy in our system, it is supposed that the negative charge brought by Al into the zeolite framework is compensated for by a positively charged SDA<sup>+</sup> molecule. Also, the microporous space of the zeolite that is formed is completely filled with organic species. This means that when the positively charged SDA<sup>+</sup> does not fill the microporous voids, neutral [SDA]<sup>+</sup>[F]<sup>-</sup> moieties (called SDA<sup>0</sup>) are located in the corresponding microporous space that is left. Therefore, the total amount of organic material  $(SDA^+ + SDA^0)$ is constant in each structure regardless of the Al content incorporated by the framework, as demonstrated by the thermogravimetric measurements and elemental analyses. Because it is not possible to model [SDA]<sup>+</sup>[F]<sup>-</sup>, the closest neutral compound is a neutralized SDA<sup>0</sup> molecule in which a fixed number of atomic charges have been added so as to make the total charge equal to zero by means of a standard averaging procedure.37

From the experimental conditions outlined, two conditions follow:

$$\frac{n}{m+n} + \frac{x}{m+n} = C \tag{14}$$

$$nAl \rightarrow nSDA^+$$
 (15)

*n* is the number of Al atoms, and this means that each Al atom is compensated by a SDA<sup>+</sup> molecule; *x* is the number of SDA<sup>0</sup> molecules, and *m* is the number of Si atoms. The condition is

fulfilled that the concentration of  $SDA^+$  plus  $[SDA]^+[F]^-$ ( $SDA^0$ ) is constant (*C*).

For two structures, eq 14 can be rewritten as

$$\frac{n_1}{m_1 + n_1} + \frac{x_1}{m_1 + n_1} = C_1$$
$$\frac{n_2}{m_2 + n_2} + \frac{x_2}{m_2 + n_2} = C_2$$

The energy per TO<sub>2</sub> (T = Si, Al) associated with eqs 13 can be written as follows:

$$\Delta E_i = \frac{E(\text{zeo}_i - \text{SDA})}{m_i + n_i} - \frac{E(\text{gel}_i)}{m_i + n_i} - \frac{n_i}{m_i + n_i} \cdot E(\text{SDA}^+) - \frac{x_i}{m_i + n_i} \cdot E(\text{SDA}^0) \quad (i = 1, 2)$$
(16)

To address our question of whether  $zeo_1$  or  $zeo_2$  is preferentially formed, the following equations have to be considered:

$$\Delta E_{\rm F} = \Delta E_2 - \Delta E_1 \tag{17}$$

 $\Delta E_{\rm F} > 0 \Longrightarrow \text{zeo}_1 - \text{SDA}$  is more stable

 $\Delta E_{\rm F} < 0 \Rightarrow zeo_2 - SDA$  is more stable

$$\Delta E_{\rm F} = \frac{E(\text{zeo}_2 - \text{SDA})}{m_2 + n_2} - \frac{E(\text{zeo}_1 - \text{SDA})}{m_1 + n_1} - \frac{E(\text{gel}_2)}{m_2 + n_2} + \frac{E(\text{gel}_1)}{m_1 + n_1} - \left(\frac{n_2}{m_2 + n_2} - \frac{n_1}{m_1 + n_1}\right) \cdot E(\text{SDA}^+) - \left(\frac{x_2}{m_2 + n_2} - \frac{x_1}{m_1 + n_1}\right) \cdot E(\text{SDA}^0)$$
(18)

The energy of the gel per  $TO_2$  unit is the same in both cases, which means that the corresponding terms vanish. Also, this process refers to different zeolites formed from the same synthesis gel, which means that the Al content is the same in both cases:

$$\frac{n_2}{m_2 + n_2} = \frac{n_1}{m_1 + n_1} \tag{19}$$

Therefore, the term containing  $E(SDA^+)$  also vanishes, and we have the following:

$$\Delta E_{\rm F} = \frac{E(\text{zeo}_2 - \text{SDA})}{m_2 + n_2} - \frac{E(\text{zeo}_1 - \text{SDA})}{m_1 + n_1} - \left(\frac{x_2}{m_2 + n_2} - \frac{x_1}{m_1 + n_1}\right) \cdot E(\text{SDA}^0) \quad (20)$$

Finally, by substituting the values of  $x_1/(m_1 + n_1)$  and  $x_2/(m_2 + n_2)$  from eqs 14 and taking into account eq 18, the final expression for  $\Delta E_F$  is obtained:

$$\Delta E_{\rm F} = \frac{E(\text{zeo}_2 - \text{SDA})}{m_2 + n_2} - \frac{E(\text{zeo}_1 - \text{SDA})}{m_1 + n_1} - \frac{(C_2 - C_1) \cdot E(\text{SDA}^0)}{(C_2 - C_1) \cdot E(\text{SDA}^0)}$$
(21)

To compare the relative stabilities of zeolites, the following structure-dependent magnitude Z is defined:

$$Z_{i} = \frac{E(\text{zeo}_{i} - \text{SDA})}{m_{i} + n_{i}} - \frac{n_{i}}{m_{i} + n_{i}} \cdot E(\text{SDA}^{+}) - \frac{x_{i}}{m_{i} + n_{i}} \cdot E(\text{SDA}^{0}) \quad (22)$$

From what has been demonstrated above, it can be seen that

$$\Delta Z = Z_2 - Z_1 = \Delta E_{\rm F} \tag{23}$$

$$\Delta E_{\rm F} > 0 \Longrightarrow \text{zeo}_1 - \text{SDA is more stable} \Longrightarrow Z_1 < Z_2 \qquad (24)$$

$$\Delta E_{\rm F} < 0 \Longrightarrow \text{zeo}_2 - \text{SDA is more stable} \Longrightarrow Z_2 < Z_1 \qquad (25)$$

From this, it follows that plotting Z for each structure versus Al content gives the relative stabilities of the different structures. Low(high) values of Z will refer to the more(less) stable structures. Also, for each structure, an interval of Al composition is defined with a minimum and a maximum value within which the structure can be synthesized. Equation 14 shows that the minimum value for Al content is zero (pure silica polimorph) and that the maximum value is C, which refers to the optimum loading of SDA<sup>+</sup> in the structure. Beyond that, further Al cannot be compensated for by any incoming SDA<sup>+</sup> molecules because all of the microporous voids are already filled.

# 5. Results and Discussion

5.1. Cation N-Cyclohexyl-N-methyl-pyrrolidinium. This SDA<sup>+</sup> (cation 1 in Scheme 2) gives mainly unidirectional zeolites. When Al<sup>3+</sup> is introduced into the reaction media (Si/ Al = 50, EU-1 is obtained within a wide range of time and temperature (Table 1). The calculated final energies (Figure 3) show that the most stable structure is ZSM-12, but the larger porosity of EU-1 allows more SDA cations to enter the pores, and for an Al content, Al/(Al + Si), in the range of [0.036, 0.055], EU-1 should be the structure that is obtained. This corresponds to a Si/Al ratio within about  $17 \le Si/Al \le 27$ , and this agrees with the results of the synthesis. The calculations have been performed with the SDA loadings indicated in Table 2, which correspond closely to the experimental loadings. These energetic considerations, based on the final energy of the product, also allow us to predict the obtaining of ZSM-12 when Al is not present in the synthesis gel, and this is especially observed when the synthesis is carried out at conditions that favor the thermodynamically stable products (longer time and higher temperature). It is clear from Table 1 that in syntheses carried out in the absence of Al the primary product is the most stable nucleus ( $\beta$  zeolite), but because of the relatively high solubility of silica (compared to silica-alumina), the primary product evolves toward the most thermodynamically stable material, which is ZSM-12 (footnote a in Table 2). Nevertheless, kinetic conditions are the most important, and when the nucleation is the determining step, the products that are formed will be those that stabilize the intermediates. This energy is calculated as the short-range interaction energy between the SDA and its closest neighbors in the microporous structure  $(E_{\text{SDA-zeo}} \text{ in Table 2})$ . It is seen that this stabilization is larger for the more open structures (-0.070 and -0.072 eV/SiO<sub>2</sub> for EU-1 and  $\beta$ , respectively) than for the monodirectional ZSM-12 (-0.045 eV/SiO<sub>2</sub>), and this explains why ZSM-12 is not the observed product when Al is introduced into the synthesis gel. Also, the higher stability of the cation in EU-1 than in  $\beta$ 



**Figure 3.** Plot of *Z* (as defined in eq 22) vs Al content for the synthesis of  $\beta$ , EU-1, ZSM-11, and ZSM-12 zeolites with cation 1 (Scheme 2). The relative final stability of different zeolites at a given Al content can be found from the graph as well as the Al composition range that allows a structure to be synthesized, which depends on the loading that the micropores can host.

(3.15 and 3.35 eV, respectively, from Table 2) allows us to predict that EU-1 should be the preferentially obtained zeolite, and this corresponds to the results of the experiments (Table 1). The term E(SDA-zeo) (Table 2) relates to a contribution that plays an important role during the nucleation stages of the synthesis. This term is mostly a short-range term between the organic cation and the zeolite surroundings, and these are precisely the interactions present when polymeric species start to form the zeolite micropore around the SDA cation. This can also explain why ZSM-11 is not the observed product in this synthesis although its energy is practically the same as that of EU-1 over the entire Al composition range (Figure 3). According to the respective contributions, -0.070 and -0.059 eV/SiO<sub>2</sub> for EU-1 and ZSM-11, respectively (Table 2), the nucleation of EU-1 would be more favorable, and the competition during the first stages of the synthesis precludes the formation of the equally stable ZSM-11 in favor of EU-1. Finally, the experiments show that  $\beta$  is the only product obtained at larger Al contents, and this is also predicted from our results in Figure 3, which show that EU-1 cannot hold more organic material in its microporous space to compensate for the Al above Al/(Al + Si) > 0.055 (that is, Si/Al < 17), which is quite close to the Si/Al ratio at which  $\beta$  appears as the only product (Si/Al < 25).

TABLE 2: Calculated Energy Terms, as Defined in Appendix 1, Involved in the Synthesis of  $\beta$ , EU-1, ZSM-11, and ZSM-12 Zeolites Obtained with the Use of SDA Cations 1 and 2 (Scheme 2)<sup>*a*</sup>

	exptl loading (org. mol/TO <sub>2</sub> )	calcd loading <sup>b</sup> (org. mol/TO <sub>2</sub> )	$E'(\mathrm{SDA}^+)^c$ (eV)	$\frac{E(\text{SDA}-\text{zeo})^d}{(\text{eV}/\text{TO}_2)}$
$\beta$ -cation 1	0.074	0.070	3.35	-0.072
EU-1-cation 1	0.056	0.054	3.15	-0.070
ZSM-11-cation 1	not observed.	0.052	3.13	-0.059
ZSM-12-cation 1	0.040	0.042	3.02	-0.045
$\beta$ -cation 2	not measured	0.047	3.46	-0.061
EU-1-cation 2	not observed	0.036	3.39	-0.053
ZSM-11-cation 2	0.045	0.042	3.13	-0.062
ZSM-12-cation 2	not observed	0.029	3.45	-0.044

<sup>*a*</sup> The energies of the calculated silica zeolite without organic occluded ( $E_1$  in Appendix 1) are -128.56, -128.59, -128.59, and -128.62 eV/SiO<sub>2</sub> for  $\beta$ , EU-1, ZSM-11, and ZSM-12, respectively. The respective calculated densities are 1.57, 1.80, 1.78, and 1.95 g/cm<sup>3</sup>. After the organic incorporation, the subsequent zeolite deformation leads to the following energies: -128.55, -128.58, -128.59, and -128.62 eV/SiO<sub>2</sub> for  $\beta$ , EU-1, ZSM-11, and ZSM-12 respectively ( $E_{zeo'}$  in Appendix 1). <sup>*b*</sup> Organic species present as SDA<sup>+</sup> (x = 0 in eq 14). Loadings correspond to *C* in eq 14. <sup>*c*</sup> Organic species present as SDA<sup>+</sup> (x = 0 in eq 14). Gas-phase energies: cation 1: 2.93 eV, cation 2: 2.91 eV. <sup>*d*</sup> Only short-range interatomic contributions included, without the electrostatic term ( $E_4 + E_5$  in Appendix 1).

5.2. Cation N-Cyclohexyl-N-butyl-pyrrolidinium. To probe the effect of the SDA cation conformation on the synthesis of zeolites, we have carried out experiments using a related organic cation such as SDA (cation 2 in Scheme 2) in which the butyl group substitutes for the methyl group in the former SDA cation. It is expected that the presence of the butyl group could discourage the formation of monodirectional channel zeolites such as EU-1 or ZSM-12. Effectively, when this cation is introduced into the synthesis gel, it gives ZSM-11 (plus  $\beta$  in some cases) in all of the syntheses that were carried out (Table 1), indicating that the larger constraint introduced as a consequence of the butyl group makes the small channels of EU-1 no longer favorable to hosting a viable loading that stabilizes its synthesis. The larger size of this SDA<sup>+</sup> causes the organic conformation to influence the synthesis process. The calculations allow us to fit loadings as indicated in Figure 4 and Table 2, again quite close to the experimental results. Although in Figures 3 and 4 the lines representing each zeolite type are very close to each other, the differences are in agreement with the experimentally measured data.<sup>2,38</sup> The final geometry of the SDA cations is very much dependent on the constraining micropore, and Table 2 shows energies above 3.45 eV for the cations in  $\beta$ and ZSM-12 zeolites, whereas only 3.13 eV is obtained in ZSM-11 (close to the absolute minimum energy of 2.91 eV). Also, as previously mentioned, the short-range interaction energy between the SDA cation and the zeolite is important to the orientation of the synthesis during the nucleation, and this term (Table 2) is more favorable in ZSM-11 and  $\beta$  zeolites (-0.062) and -0.061 eV/TO<sub>2</sub>, respectively) than in EU-1 and ZSM-12  $(-0.053 \text{ and } -0.04 \text{ eV/TO}_2, \text{ respectively})$ . Therefore, from the above considerations, ZSM-11 and  $\beta$  should be the synthesis products, and this is exactly what is found in the experiments (Table 2). Although the stabilization coming from the shortrange interaction energy points toward both ZSM-11 and  $\beta$  as synthesis products, we think that the observed preferential synthesis of ZSM-11 is due to the fact that the SDA cation is more relaxed inside ZSM-11 than in  $\beta$ , as shown by the respective energies of 3.13 and 3.46 eV (Table 2). The shape of the micropores of ZSM-11 seems to be more suited than the other structures to host this bulkier cation. However, the possibility of the  $\beta$  zeolite forming does exist despite the higher energy required for the SDA cation to adopt a conformation suited to the micropore shape. This high-energy conformation will require a larger activation energy for the corresponding nucleus to be formed. Again, as in the previous case with cation 1, the use of pure silica gels allows a higher solubility, and the primary products in the competitive reactions (kinetic model



**Figure 4.** Plot of *Z* (as defined in eq 22) vs Al content for the synthesis of  $\beta$ , EU-1, ZSM-11, and ZSM-12 zeolites with cation 2 (Scheme 2). The relative final stability of different zeolites at a given Al content can be found from the graph as well as the Al composition range that allows a structure to be synthesized, which depends on the loading that the micropores can host.

in Figure 2, middle) evolve toward the most stable structure between the competing products ( $\beta$  and ZSM-11), which is ZSM-11 (footnote a in Table 2). Previous studies have proposed that template configurations occluded in the microporous voids are similar to the equilibrium.<sup>39</sup> Our model supports this hypothesis with the corolary that reaction temperatures always allow a significant degree of deformation of the SDA organic

## 6. Conclusions

Short-range energy interactions are the dominating, albeit not the only, factor that orients the zeolite synthesis. Thermodynamic factors determine only when the activation energies of the synthesis steps are low enough for the competitive reactions to take place, and this occurs at long time, high temperature, and high solubility. Therefore, from the two energetic schemes outlined in this study, the analysis of energetic terms seems to be more appropriate than the plotting of the defined Z function.

The energetic terms corresponding to the short-range interaction between the zeolite and the charge SDA play an important role during the nucleation stage, and the zeolite synthesis may be mainly driven by this interaction. In such a case, the results can be explained in terms of the stability of the appropriate nuclei during the initial stages of the zeolite formation.

In the case of the synthesis with the *N*-methyl-*N*-cyclohexylpyrrolidinium cation, ZSM-12 (the most stable zeolite) is the product obtained when the synthesis is carried at conditions that favor the thermodynamically stable products and without Al, which by making the gel more soluble allows the competitive reactions to drive the products toward the more thermodynamically stable. As the Al content increases, EU-1 becomes the favored product because of the favorable zeolite–SDA<sup>+</sup> interactions and the low SDA<sup>+</sup> energy. At even larger Al content, EU-1 cannot hold the necessary organic to compensate for Al, and  $\beta$ becomes the observed product because of a favorable zeolite– SDA<sup>+</sup> interaction.

The conformation of the occluded organic cation inside the zeolite is an important parameter. Zeolite structures that force the occluded SDA<sup>+</sup> to adopt a conformation far from that of the equilibrium conformation in solution are not favored. Nevertheless, flexible templates may offer a wide range of conformations that can be reached under these synthesis conditions. Butyl cations can adopt a conformation that orientates the synthesis toward  $\beta$ . In most cases, the more favored conformation and more stable nucleus leading to ZSM-11 is the observed product.

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### Appendix 1

We consider three contributions to the energy of the final system zeolite $-SDA^+$ : (i) the stability of the structure ( $E_{zeo}$ ); (ii) Al incorporation into the zeolite framework, which is expected to take different energetics according to the flexibility,

topology and Al location  $(E_{Si \rightarrow Al})$ ; (iii) the incorporation of the SDA into the microporous voids, which produces four energetic effects: modifies its conformation with respect to the equilibrium ( $\Delta E_{SDA^+}$ ), stabilizes the zeolite-SDA interactions through short-range and long-range terms ( $E_{zeo-SDA^+}$ ), increases the framework energy ( $E_{zeo'}$ ), and SDA<sup>+</sup>-SDA<sup>+</sup> interactions between the occluded organic appear ( $E_{SDA^+-SDA^+}$ ). SDA<sup>+</sup>-SDA<sup>+</sup> interactions depend strongly on the number of SDA<sup>+</sup> molecules hosted in the zeolite lattice, and the optimum loading is reached when a compromise is reached between the repulsive SDA<sup>+</sup>-SDA<sup>+</sup> interactions (which preclude excessive loading) and the attractive zeolite-SDA<sup>+</sup> terms (which avoid loadings that are too low). For the calculations of the energy terms, the GULP code has been used, and the geometry of the organic cations and the zeolite structures has been optimized with the procedures used in previous work.<sup>35</sup> The energy decomposition has been possible by taking the final geometry and calculating the individual contributions of the corresponding force field acting on the involved atoms. A more detailed analysis of each contribution follows.

• A fundamental role is played by the structural type that crystallizes from the synthesis gel. The size and shape of the microporous voids determine the framework density, which correlates with the enthalpy of formation to a large extent.<sup>27,38,40,41</sup> The comparison between different structural types has to be performed with equal compositions, hence SiO<sub>2</sub> structures are used for this purpose. Optimized silica structures can be easily calculated within our computational methodology, and energy difference between the initial gel and the crystallized zeolite can be calculated by taking only the energy of the optimized zeolite to estimate relative energies because the different structures in our experiments crystallize from the same synthesis gel, which is taken as our zero of energy. Hence,  $E_1 = E_{zeo-Si}$ . The corresponding energies appear in Table 2.

• Different abilities of a given structural type to incorporate aluminum in the framework can be expected. An estimation of this can be achieved by using the Mott-Littleton methodology<sup>35</sup> to calculate defect energies. Although Al incorporation should not be expected to remain constant as Al content increases, a simplication can be made when incoming Al atoms are located far apart and are nearly noninteracting. In that case, an average over the different T sites can give a reasonable approximation. Calculating the average defect energy,  $E_{Si \rightarrow Al}$ , will give us the total energy needed to accommodate Al atoms as  $E_2 =$  $\Delta E_{\text{Al incorporation}} = n E_{\text{Si} \rightarrow \text{Al}}$ , where *n* is the number of Al atoms incorporated, which should be small enough to make Al-Al interaction negligible. The average Mott-Littleton energies (in eV) related to the Al incorporation for the considered structures are 38.1 (β), 38.4 (EU-1), 38.3 (ZSM-11), and 38.5 (ZSM-12). The standard deviation is below 0.1 eV in all cases.

• SDA<sup>+</sup> molecules deform when entering the zeolite microcavities, thus increasing the energy of the former with respect to the equilibrium energy. The difference in energy can be calculated from the corresponding energies within the zeolite cage  $(E'_{\text{SDA}^+})$  and in the equilibrium free state  $(E_{\text{SDA}^+})$  as follows:  $E_3 = \Delta E_{\text{SDA}^+} = E'_{\text{SDA}^+} - E_{\text{SDA}^+}$ . This term is shown to be an important influence on the synthesis process because during the nucleation process SDA<sup>+</sup> cations have to adopt a conformation that matches the channel/pore of the zeolite to be formed. If this is a high-energy conformation, then only when the associated activation energy is overcome will this zeolite synthesis be possible. The flexibility of the SDA<sup>+</sup> is an important issue because flexible molecules can give several structures at the expense of losing template ability, that is, the specificity to direct the synthesis toward a particular structure. Therefore, templates have to be rigid molecules. Table 2 shows the energies of  $SDA^+$  cations in the different zeolites considered and in the gas phase.

• Entering into the zeolite also has an effect of stabilization due to the interaction with the zeolite walls, where mainly the oxygen atoms, which are closer to the guest molecule than to the T atoms, stabilize the positively charged SDA<sup>+</sup> ( $E_4 =$  $E_{SDA^+-zeo}$ ). This can be calculated from the corresponding Lennard-Jones plus electrostatic terms between the zeolite and the SDA<sup>+</sup> (see eq 5). This term is related to the energetics of the nucleation because it takes into account not only the SDA<sup>+</sup> conformation around which the zeolite grows but also its major contribution that is made by the silicate units closer to the SDA<sup>+</sup>. Similarly, SDA<sup>+</sup>-SDA<sup>+</sup> interactions appear when several molecules are occluded within channels or cavities ( $E_5 =$  $E_{\text{SDA}^+-\text{SDA}^+}$ ). This repulsive energy between positively charged SDA<sup>+</sup> molecules can be calculated from the Lennard-Jones and electrostatics terms as indicated in eq 4. Table 2 shows the corresponding energies  $(E_4 + E_5 = E_{SDA^+-zeo} + E_{SDA^+-SDA^+})$ for the two organic cations considered in  $\beta$ , EU-1, ZSM-11, and ZSM-12 structures. The dominant contribution is  $\Delta E_4$ , which amounts to at least 90% of the total Lennard-Jones shortrange contributions between the zeolite and the organic cations.

• The zeolite will be higher in energy than when isolated because of the deformation of the framework produced by the incorporation of the SDA<sup>+</sup> ( $E_6 = \Delta E_{zeo}$ ). This term can be calculated from the final geometry of the system by taking off the SDA molecules, calculating the energy of the corresponding "stressed" zeolite ( $E_{zeo'}$ ), and subtracting the energy of the isolated zeolite ( $E_{zeo'}$ ). Finally,  $\Delta E_{zeo} = E_{zeo'} - E_{zeo}$ . The corresponding energies of  $\beta$ , EU-1, ZSM-11, and ZSM-12 are shown in Table 2.

#### **References and Notes**

- (1) Davis, M. E.; Lobo, R. F. Chem. Mater. 1992, 4, 756.
- (2) Petrovic, I.; Navrotsky, A.; Davis, M. E.; Zones, S. I. Chem. Mater. 1993, 5, 1805.
  - (3) Annen, M. J. Microporous Mater. 1993, 1, 57.
- (4) Corma, A.; Navarro, M. T.; Rey, F.; Valencia, S. Chem. Commun. 2001. 16, 1486.
- (5) Corma, A.; Navarro, M. T.; Rey, F.; Rius, J.; Valencia, S. Angew. Chem., Int. Ed. 2001, 40, 2277.
  - (6) Barrer, R. M. Zeolites 1981, 1, 130.
  - (7) Barrer, R. M. Stud. Surf. Sci. Catal. 1985, 24, 1.
  - (8) Lok, B. M.; Cannan, T. R.; Messina, C. A. Zeolites 1983, 3, 282.
  - (9) Davis, M. E. Acc. Chem. Res. 1993, 26, 111.
- (10) Hong, S. B.; Cho, H. M.; Davis, M. E. J. Phys. Chem. 1993, 97, 1622.
- (11) Corma, A.; Diaz-Cabañas, M. J.; Fornes, V. Angew. Chem., Int. Ed. 2000, 39, 2346.
- (12) Lewis, D. W.; Freeman, C. F.; Catlow, C. R. A. J. Phys. Chem. B 1995, 99, 11194.

- (13) Lewis, D. W.; Catlow, C. R. A.; Thomas, J. M. Chem. Mater. 1996, 8, 1112.
- (14) Toby, B. H.; Khosrovani, N.; Dartt, C. B.; Davis, M. E.; Parise, J. B. *Microporous Mesoporous Mater.* **2000**, *39*, 77.
- (15) Catlow, C. R. A.; Coombes, D. S.; Lewis, D. W.; Pereira, J. C. G. Chem. Mater. 1998, 10, 3249.
- (16) Lewis, D. W.; Sankar, G.; Wyles, J. K.; Thomas, J. M.; Catlow, C. R. A.; Willock, D. J. Angew. Chem., Int. Ed. Engl. 1997, 36, 2675.
- (17) van de Graaf, B.; Njo, S. L.; Smirnov, K. S. Rev. Comput. Chem. 2000, 14, 137.

(18) Wagner, P.; Nakagawa., Y.; Lee, G. S.; Davis, M. E.; Elomari, S.; Medrud, R. C.; Zones, S. I. J. Am. Chem. Soc. **2000**, 122, 263.

(19) Shantz, D. F.; Lobo, R. F.; Fild, C.; Koller, H. Stud. Surf. Sci. Catal. 2000, 130, 845.

(20) Shantz, D. F.; Schmedt auf der Günne, J.; Koller, H.; Lobo, R. F. J. Am. Chem. Soc. 2000, 122, 6659.

(21) Shantz, D. F.; Fild, C.; Koller, H.; Lobo, R. F. J. Phys. Chem. B 1999, 103, 10858.

(22) Sabater, M. J.; Sastre, G. Chem. Mater. 2001, 12, 4520.

(23) Borch, R. F.; Bernstein, M. D.; Dupont Durst, H. J. Am. Chem. Soc. 1971, 93, 2897.

(24) Gale, J. D. J. Chem. Soc., Faraday Trans. 1997, 93, 629.

(25) Sanders, M. J.; Leslie, M.; Catlow, C. R. A. J. Chem. Soc., Chem. Commun. 1984, 1271.

(26) Jackson, R. A.; Catlow, C. R. A. Mol. Simul. 1988, 1, 207.

(27) Henson, N. J.; Cheetham, A. K.; Gale, J. D. Chem. Mater. 1994, 6, 1647.

- (28) Henson, N. H.; Cheetham, A. K.; Gale, J. D. Chem. Mater. 1996, 8, 664.
- (29) Modelling of Structure and Reactivity in Zeolites; Catlow, C. R. A., Ed.; Academic Press: London, 1992.
- (30) Catlow, C. R. A.; Bell, R. G.; Gale, J. D. J. Mater. Chem. 1994, 4, 781.

(31) Kiselev, A. V.; Lopatkin, A. A.; Shulga, A. A. Zeolites 1985, 5, 261.

- (32) Oie, T.; Maggiora, T. M.; Christoffersen, R. E.; Duchamp, D. J. Int. J. Quantum Chem., Quantum Biol. Symp. 1981, 8, 1.
- (33) Ditchfield, R.; Hehre, W. J.; Pople, J. A. J. Chem. Phys. 1971, 54, 724.

(34) Harrison, R.; Nichols, J.; Straatsma, T.; Dupuis, M.; Bylaska, E.; Fann, G.; Windus, T.; Apra, E.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; de Jong, B.; Deegan, M.; Dyall, K.; Elwood, D.; Fruchtl, H.; Glendenning, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kendall, R.; Kobayash, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nieplocha, J.; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; van Lenthe, J.; Wolinski, K.; Wong, A.; Zhang, Z. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 4.0; Pacific Northwest National Laboratory: Richland, WA, 2000.

(35) Sastre, G.; Lewis, D. W.; Catlow, C. R. A. J. Phys. Chem. 1996, 100, 6722.

(36) Sastre, G.; Fornes, V.; Corma, A. J. Phys. Chem. B 2002, 106, 701.

(37) Rappe, A. K.; Goddard, W. A., III. J. Phys. Chem. 1995, 95, 3358.

(38) Piccione, P. M.; Laberty, C.; Yang, S.; Camblor, M. A.; Navrotsky, A.; Davis, M. E. J. Phys. Chem. B 2000, 104, 10001.

- (39) Davis, M. E. *CATTECH* **1997**, *1*, 19.
- (40) Akporiaye, D. E.; Price, G. D. Zeolites 1989, 9, 321.
- (41) Kramer, G. J.; de Man, A. J. M.; van Santen, R. A. J. Am. Chem. Soc. 1991, 113, 6435.