

Mechanism of Dichlorination of *n*-Dodecane and Chlorination of 1-Chlorododecane Adsorbed on ZSM-5 Zeolite Molecular Sieves. A Supramolecular Structural Interpretation[▽]

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Abstract: The product distributions produced by the photoinduced dichlorination of *n*-dodecane (nD) and the photoinduced monochlorination of 1-chlorododecane (1CD) adsorbed on two pentasil zeolites (silicalite and LZ-105) have been investigated. The results are explained in terms of a supramolecular model for which the mobile and diffusing chlorination reagents (Cl[•]/Cl₂) enter the zeolite particle from the external surface and diffuse preferentially along the linear channels of the zeolite internal surface that contain immobile adsorbed nD (or 1CD) molecules. The model assumes that the outermost layer of adsorbed substrates is attacked preferentially, that the attack occurs at the proximal end of adsorbed nD molecules closest to the external surface, and that, after the first chlorination, the substrate molecules in an inner layer are protected from chlorination by "blocking" molecules parked in the outer layer. The model describes each substrate molecule adsorbed on the internal surface in terms of supramolecular isomeric structures that are capable of characterizing the specific void space sites occupied by the substrate. A detailed analysis of the results allows the conclusion that the compensating cations tend to be preferentially located in the zigzag channels rather than in the linear channels or intersections and that the variation of selectivity of chlorination with experimental conditions results from redistribution of the isomeric supramolecular structures.

Introduction

Zeolites are crystalline inorganic polymers whose constitution consists of corner-sharing AlO₄ and SiO₄ tetrahedra which form a 3D framework.¹ The rigid framework structure encapsulates an intracrystalline void space of channels, pores, and cages that are accessible to guest molecules capable of diffusing from the external surface into the intracrystalline surface. The enormous internal surface area (typically ca. 500–1000 m²/g) of zeolites is capable of high selectivity of adsorption of molecules of appropriate size and shape, and the high thermal stability and outstanding catalytic ability of zeolites place them as one of the most important classes of materials employed for industrial catalysis, e.g., the catalysis of petroleum formation and cracking processes.

The pentasils are a family of high-silica zeolites possessing an internal framework of intersecting channels whose 10-membered rings, created by Si,Al-centered tetrahedra, control the size of the pores and the internal void space of the crystal and therefore control the size and shape of molecules able to penetrate and diffuse through the internal surface.² LZ-105 and silicalite are representative members of the pentasil family of zeolites and are related to the important industrial family of ZSM-5 zeolites, which are well-known for their outstanding size/

shape-sensitive catalytic characteristics.³ Although LZ-105 and silicalite possess identical internal void space morphologies, LZ-105 has a relatively high Al content for a pentasil (Si/Al ca. 20) and silicalite contains the lowest Al content of any pentasil zeolite (Si/Al > 1000).

Their practical importance aside, zeolites possess fascinating structural features as "microscopic restricted spaces" for chemical reactions and as such are excellent hosts for the investigation of the role of size–shape features in determining the effects of reactions in restricted spaces.⁴ The remarkable catalytic properties and outstanding size/shape adsorptive selectivity characteristics of pentasil zeolites³ provide a tremendous incentive and motivation for basic research that will further the understanding of the connection between the pentasil void space structure, the sitings of substrates in the accessible void space, and catalytic properties. Details concerning the siting of adsorbed molecules, the dynamics of exchange of adsorbed molecules between sites, and the number and location of active sites are critical issues to be addressed by fundamental investigations. Another important issue is the role of the Si/Al ratio in determining the

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[▽] Dedicated to Professor Dr. Hans-Dieter Scharf on the occasion of his 65th Birthday.

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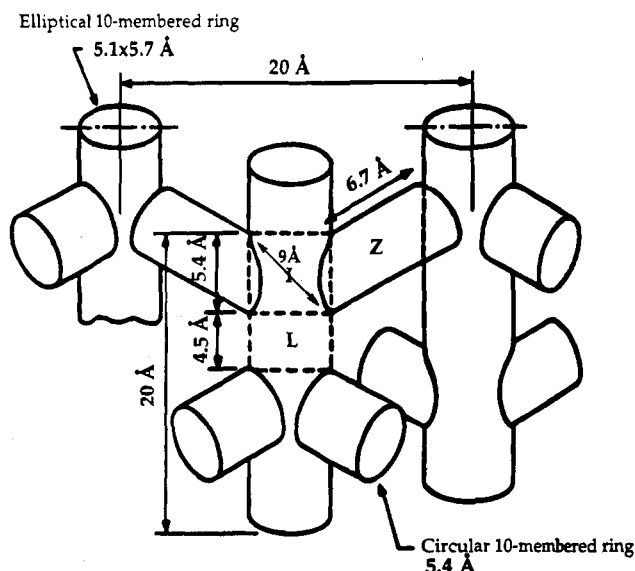


Figure 1. Three-dimensional representation of the internal void system of a portion of crystalline pentasil zeolite. The entire void system can be viewed as consisting of various periodic combinations of three atomic void units: (1) an intersection, I; (2) a zigzag channel, Z; and (3) a linear channel, L. The dimensions of these units and the length of a unit cell are given in the figure.

catalytic and adsorptive properties of pentasils, since this ratio can be varied over several orders of magnitude and the number of Al atoms is generally agreed to be equal to the number of active sites.⁵ These issues have all been addressed theoretically⁶ but have not been definitively established experimentally.

In addition to these structural issues, an understanding of the dynamics of diffusion of reagents and substrates throughout the void space presents the possibility of the fascinating phenomena of "molecular traffic control" of catalytic reactions.⁷ The traffic metaphor elicits microscopic analogies of "parking problems" as a function of sites occupied and of "traffic jams along the diffusional highway". We shall keep these metaphors in mind since the ideas of mass transport are very effective as a basis for interpreting the results.

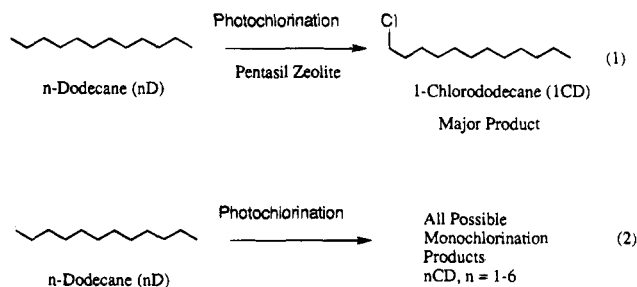
Finally, since photochemical excitation at or near room temperature is being employed in our investigations, complications due to the high temperatures commonly employed to examine the catalytic properties of zeolites are avoided and the size-shape and diffusional aspects of catalytic action are emphasized.

Quantitative Aspects of the Pentasil Intracrystalline Void Space. The unit cell of a pentasil zeolite² contains 96 interconnected tetrahedral atoms (Al or Si). Silicalite, the "aluminum-free" end member of the pentasil family of zeolites, possesses a composition of 96 SiO₂ per unit cell. From the X-ray structure of silicalite,² the topology of the intracrystalline void space has been established (Figure 1). The void space of silicalite consists of a system of intersecting channels composed of zigzag channels (roughly circular, ca. 5.5 Å cross section, labeled Z in Figure 1) and straight or linear channels (roughly elliptical, ca. 5.4 × 5.1 Å cross section, labeled L in Figure 1). The Z and L void space units meet at intersections (roughly spherical, ca. 9 Å diameter, labeled I in Figure 1). At saturation, the void space available for molecules that can fit into the internal surface is remarkable, ca. 0.2 cm³/g.

The LZ-105 pentasil possesses a unit cell morphology that is identical to that of silicalite but possesses a Si/Al ratio of about 20/1, corresponding to an average of 5 Al atoms per unit cell. From the known structure of pentasils, this corresponds to ca. 1 Al atom per intersection. Each tetrahedral Al atom carries with it a formal negative charge and therefore an obligatory compensating cation. From these structural considerations, for each combination of a linear channel, zigzag channel, and intersection, there is, on the average, a cation in or near the channels (L or Z) or intersections (I).

The pentasil zeolites possess the important characteristic of adsorbing and selectively cracking linear hydrocarbons.⁸ Critical issues are the fraction of void space that is accessible to adsorbents such as linear hydrocarbons and the number and favorable sites for adsorption per unit cell. We are concerned in this paper with the supramolecular structure and dynamics of *n*-dodecane (nD) and 1-chlorododecane (1CD) molecules adsorbed on the internal surface of pentasil zeolites. In particular, we examine the influence of adsorption of molecules within this void space on the selectivity of product formation in the photochlorination of nD and 1CD molecules that are adsorbed on the **internal surface** of pentasils. The unit cell of a pentasil zeolite contains three unique void spaces (I, L, and Z described above) that are formally accessible for portions of nD or 1CD molecules (Figure 1). We shall consider below a method of describing a set of supramolecular structures whose "atomic" units are three connected void spaces (I, L, and Z of the host structure) and the nD molecules (ends and center of the guest structure). A related set of structures will pertain to 1CD adsorbed in pentasils.

Previous Results on the Photochlorination of *n*-Dodecane Adsorbed on Pentasils. We have reported an investigation⁹ of the monochlorinated products produced by the photochlorination of nD adsorbed on pentasil zeolites and have found that under a variety of conditions the course of photochlorination proceeds with a high selectivity to produce 1CD (eq 1). This



result contrasted dramatically with that of the photochlorination of *n*-dodecane in solution, which proceeds with negligible selectivity; i.e., in solution photochlorination of nD all of the monochlorododecanes are produced in comparable amounts (eq 2).

The maximum coverage by nD of the internal surface of a pentasil zeolite corresponds to less than ca. 10% w/w loading.⁸ For loadings of more than ca. 10%, the "excess" nD is adsorbed on the external surface. In the *monochlorination* of nD adsorbed on NaLZ-105, the maximum selectivity for terminal chlorination occurred for coverages of ca. 50%, corresponding to ca. 3–4% loading. These loadings, correspond to ca. one dodecane molecule per unit cell. Since photochlorination of nD on the

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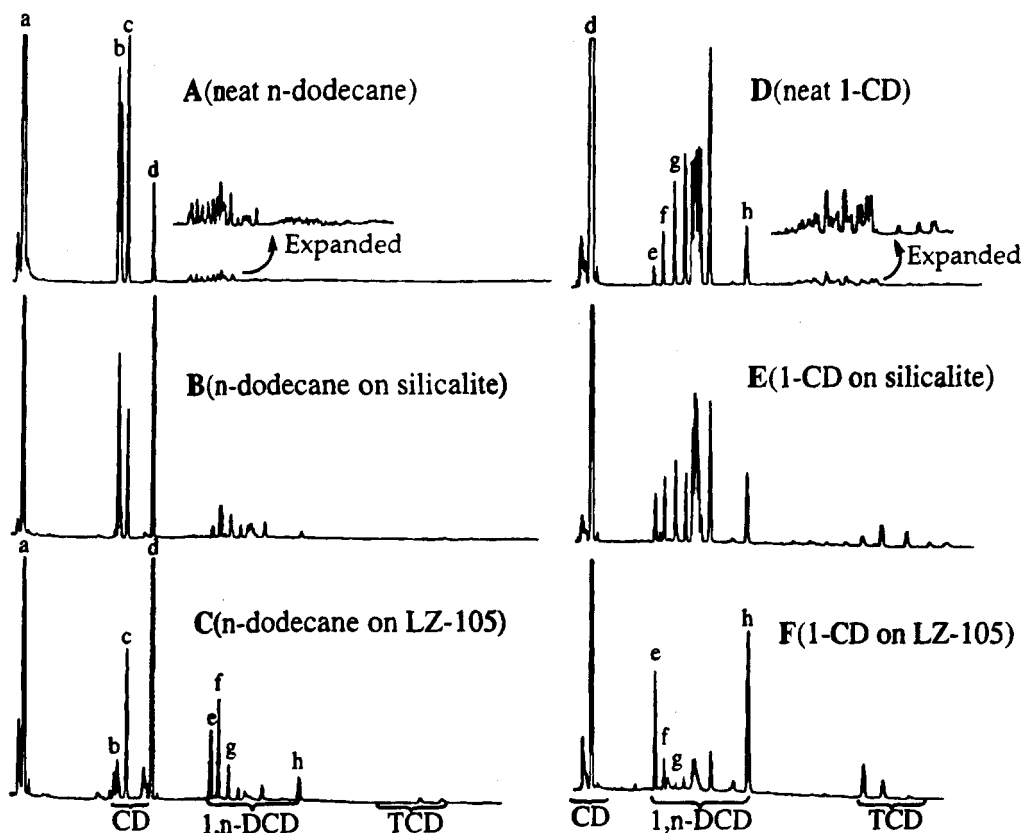


Figure 2. Representative gas chromatograms of the products produced in the photochlorination of *n*-dodecane (nD, left) and 1-chlorododecane (1CD, right) under various conditions (see text for details): (A) neat nD; (B) nD adsorbed on silicalite; (C) nD adsorbed on LZ-105; (D) neat 1CD; (E) 1CD adsorbed on silicalite; (F) 1CD adsorbed on LZ-105. The products that have been identified are labeled with letters: (a) nD; (b) 4-, 5-, and 6CD; (c) 2- and 3CD; (d) 1CD; (e) 1,1DCD; (f) 1,2DCD; (g) 1,3DCD; (h) 1,12DCD. The times of elution of the three chromatograms on the left are identical to each other as are the times of elution of the three chromatograms on the right. However, the chromatogram on the right was taken with a higher temperature profile to emphasize the dichlorinated and trichlorinated product profiles.

external surface is characterized by low terminal selectivity, at loadings of ca. 10% and higher, the terminal selectivity is expected and found to drop rapidly.⁹

The salient results for the monochlorination of nD adsorbed on NaLZ-105 at less than 10% coverage (i.e., conditions such that nearly all of the adsorbed nD molecules cover the internal surface) were⁹ as follows: (1) 1-chlorododecane (1CD) was always the major product under a variety of conditions; (2) the selectivity for formation of 1CD was dependent on percent loading and reached a maximum selectivity at a few percent loading; (3) the selectivity for formation of 1CD was insensitive to the charge of chlorine gas employed; (4) there is a modest selectivity for internal chlorination (the sum of C-2 and C-3 versus the sum of C-4, C-5, and C-6); (5) for a given coverage, the terminal selectivity of chlorination was similar to that for nD for *n*-nonane, tridecane, and octadecane. These results were consistent with a structural model in which nD molecules mainly occupy the linear channels of the zeolite at loadings corresponding to less than 10% and in which the reagent chlorine atoms and chlorine molecules mainly diffuse into the intracrystalline internal surface from the external surface and then diffuse up and down the linear channels.

We report here the influence of the compensating cation in the pentasil structure on the selectivity of monochlorination of nD. Along with earlier results, these new results are explained in terms of a supramolecular structural model of a host-guest complex which takes into account the following features: (1) the reactive regions within a single crystal; (2) the configurations of adsorbed molecules within the reactive regions; (3) the distribution of these configurations among the L, I, and Z sites; (4) the orientations of these configurations with respect to the

external surface; and (5) the diffusional pathways available to the reagents. We also report here the influence of the compensating cation on the dichlorination products of nD. Finally, we report the comparison of the monochlorination products of 1CD adsorbed on NaLZ-105 to the dichlorination products of nD adsorbed on NaLZ-105. We shall show that the results of the dichlorination of nD and the monochlorination of 1CD can be interpreted in terms of the same structural model employed to explain the striking terminal selectivity observed in the monochlorination of nD and that the results provide support for the molecular traffic control model⁷ for reagent diffusion in the pentasil structure.

Results

Product Distributions. General Observations. It was found that in the range of 1–10% loading (ca. 5–100% coverage of the internal surface), the rate of formation of all chlorinated products decreases as a function of conversion. Two other important general observations are that (1) dichlorinated products are formed in significant amounts even at relatively low conversions and (2) even at the maximum limit of conversion considerable amounts of nD are either not chlorinated or chlorinated very slowly.

Figure 2 shows a representative set of gas chromatograms displaying the product profiles for the photochlorination of nD and 1CD as neat liquids (Figure 2, parts A and D, respectively), as substrates adsorbed on silicalite (Figure 2 parts B and E, respectively), and as substrates adsorbed on NaLZ-105 (Figure 2, parts C and F, respectively). Under representative conditions (loading of 3–4%, conversion to ca. 50% of the maximum limit,

ambient temperature), the product distributions contain typically ca. 75% monochlorinated products (CDs, Figure 2) and ca. 25% dichlorinated products (DCDs, Figure 2) and only traces (<2–3%) of trichlorinated products (TCDs, Figure 2).

The product distributions were found to have only a slight dependence on the method of depositing the substrates onto the zeolite. For example, deposition from isooctane (a solvent whose size and shape prevent it from being readily adsorbed into the internal surface) or deposition from *n*-pentane (a solvent that is simultaneously adsorbed with *n*D but is readily removed after deposition of *n*D on the internal surface) leads to comparable product distributions. The results reported here refer to deposition of *n*D from *n*-pentane, since this procedure is more representative of common practice in the field for depositing molecules on zeolites. The retention times of the monochlorinated products were all determined by comparison to standard samples available commercially or synthesized according to established procedures (see Experimental Section). Of the monochlorination products (Figure 2, left), the 2- and 3-isomers elute with similar retention times and are not resolved and thus are given the single label c; similarly the 4-, 5-, and 6-isomers are not resolved and are given the single label b. However, the 1CD isomer (labeled d) is clearly separated from all of the other isomers.

Among the dichlorination products, 1,1DCD, 1,2DCD, and 1,12DCD (Figure 2e,f,h, respectively) were identified unambiguously by comparison with standard samples available commercially or synthesized according to established procedures (see Experimental Section). A trace product in all of the photochlorinations which elutes immediately after 1,2DCD was identified tentatively as 1,3DCD (Figure 2g). From the gas chromatographic analyses it appears that the retention times of the 1,*n*DCDs (*n* = 1–12) increase in approximately the same order as the value of *n*, i.e., 1,1DCD elutes first, followed by 1,2DCD, etc., and 1,12DCD (Figure 2h) elutes last.

Importantly, it was found that, in general, the same set of DCDs is produced from the **dichlorination of *n*D in situ** and from the **monochlorination of 1CD**. Since all DCDs produced from monochlorination of 1CD must be 1,*n*DCDs, *all of the DCDs produced from the dichlorination of *n*D in situ also must be 1,*n*DCDs (*n* = 1–12)*. From the number of resolved peaks in the region of elution of the DCDs, it appears that all 12 possible 1,*n*DCDs are produced, but the majority of the product profile corresponds to a mixture of *n* = 1, 2, 3, and 12 for nearly all conditions investigated. Other isomers of dichlorododecane (*m,n*DCD with *n* ≠ 1) are produced only in trace amounts.

Although no attempt was made to characterize the trichlorododecanes (Figure 2, TCDs), it is clear from the chromatograms that the trichlorination for the photochlorination of *n*D in the zeolite systems is highly selective compared to the photochlorination of *n*D as a neat system (Figure 2A).

Selectivity Parameters. Several selectivity parameters¹⁰ will be defined to analyze conveniently and systematically the complicated product distributions (which may be viewed as "product spectra" characteristic of the details of the supramolecular structure and dynamics of the chlorination) such as those shown in Figure 2 as a function of experimental variables (loading, cation structure, temperature, etc.).

A parameter for the selectivity of terminal chlorination, S_t , refers to the ability of the reagents (Cl_2/Cl^*) to monochlorinate the terminal methyl groups in preference to any of the internal methylene groups. S_t is defined so that a value of 1.0 means no selectivity on a per hydrogen basis and a value greater than

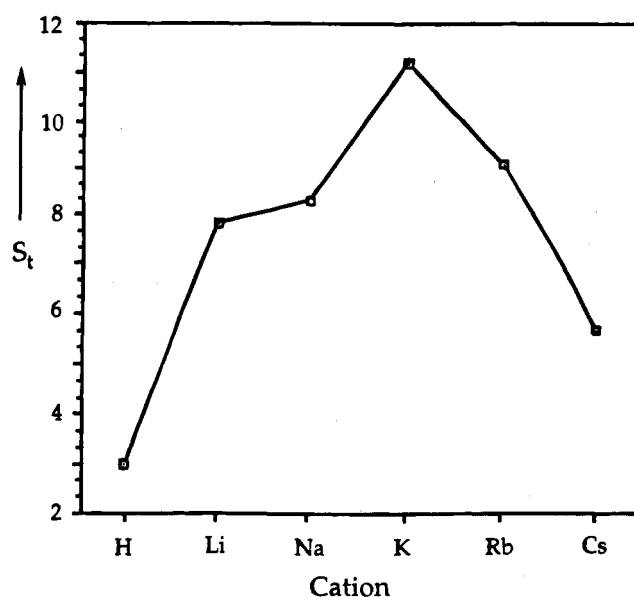


Figure 3. Terminal selectivity, S_t , vs the compensating cation, *M*, for photochlorination of *n*D adsorbed at ca. 4% loading on MLZ-105. See text for discussion.

1 implies a preference for chlorination on a per hydrogen basis. Thus, the experimental parameter, S_t , provides a quantitative measure of the selectivity (based on the product distribution of monochlorinated products), on a per hydrogen basis, for terminal monochlorination at methyl carbons relative to chlorination of each of the methylene carbons. It is expected that the value of S_t will scale as the number of collisions of the reagents with the methyl and methylene groups of the adsorbed substrate.

Selectivity of secondary chlorination of the methylene groups, S_i , is defined as the ratio of the average selectivity for chlorination at carbons 2 and 3 (both fall under peak b in Figure 2) relative to that for carbons 4–6 (all three fall under peak c in Figure 2) on a per hydrogen basis. This parameter provides information concerning the selectivity of chlorination of methylenes near the ends of an *n*D molecule (carbons 2 and 3) compared to chlorination of methylenes near the center of an *n*D molecule (carbons 4–6).

The selectivity for monochlorination (relative to dichlorination and polychlorination) at a given conversion is given by S_m and is defined simply as the percent of monochlorination of *n*D versus the total amount of *n*D reacted. This parameter provides information concerning the ease and extent of monochlorination as a function of reaction conditions.

Effect of Loading on Selectivity in the Monochlorination of *n*D. For various metal cations, the maximum value of S_t was in the range 8–11 as a function of loadings in the range of 1–10% (Figure 3). For example, the maximum values of S_t were found at loadings of ca. 2–4% for the five alkali cations (Li, Na, K, Rb, and Cs) investigated. The values of S_t tend to decrease modestly (i.e., the chlorination becomes less selective) at loadings greater than ca. 6% and then drop off dramatically at loadings of greater than ca. 8–10%. This result is expected if the maximum internal coverage has been achieved at ca. 8% loading because at this point the external surface becomes covered to an ever greater extent with further loading and because the photochlorination of *n*D adsorbed on the external surface is expected to be nonselective, as it is in solution. For example, for NaLZ-105, the values of S_t are 7.4, 8.3, 5.8, 3.3, and 2.4 for 2%, 4%, 6%, 8%, and 10% loadings, respectively. However, for loadings less than ca. 8%, the drop-off in selectivity is not expected to be due to molecules on the external surface.

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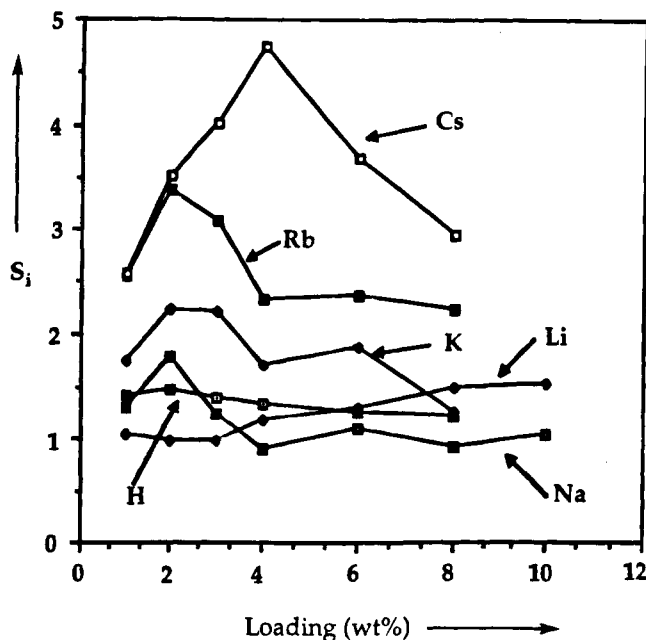


Figure 4. Secondary selectivity, S_i , vs loading for the photochlorination of nD adsorbed on MLZ-105. See text for discussion.

The parameter S_i was relatively insensitive to loading for small cations (H, Li, and Na, Figure 4) but significantly more sensitive to loading for larger cations (K, Rb, and Cs, Figure 4). In the case of the larger cations a significant maximum in the profile of S_i versus loading is observed.

The value of S_m is ca. 80% and is relatively insensitive to loading for small cations (H, Li, and Na) but increases with increasing loading for the larger cations (K, Rb, and Cs). The DCDs consist essentially only of 1,nDCDs with only traces of m,nDCDs ($m \neq 1$). A comparison of parts A and C of Figure 2 reveals that a much larger number of DCDs is produced in the neat photochlorination compared to the photochlorination of nD adsorbed on a pentasil zeolite.

We note that these characteristics are neither expected nor observed for chlorination of nD molecules adsorbed on the external surface. Thus, the selectivity parameters demonstrate that at loadings of less than 8% essentially all of the photochlorination results from reaction of nD molecules adsorbed on the internal surface.

Effect of Compensating Cation on Terminal Selectivity in the Monochlorination of nD at Fixed Loading. At a fixed loading of ca. 4%, the parameter S_i is a function of the compensating cation (Figure 3). When silicalite (which contains a negligible number of cations in its internal surface) and HLZ-105 (which contains small cations in its internal surface) are employed as host zeolites, the value of S_i is lower (ca. 2–3) at this fixed loading. Thus, the occurrence of cations larger than H^+ (i.e., metal cations) within the void space significantly enhances the selectivity for terminal chlorination. In the case of K as the compensating cation the yield of 1CD in the reaction mixture reaches ca. 80% ($S_i > 10$, Figure 3).

Effect of Temperature on Terminal Selectivity, S_i , in the Monochlorination of nD. For nD/NaLZ-105 at a fixed loading of ca. 3%, values of S_i from ca. 7 to 9 and of S_m from ca. 70% to 80% were observed over the temperature range 24–73 °C. Thus, neither S_i nor S_m is significantly influenced by temperature variation at a fixed loading typical of the systems investigated.

Effect of Coadsorbed Molecules on the Terminal Selectivity, S_i , in the Monochlorination of nD. At a fixed loading of ca. 4%, the addition of pyridine as a coadsorbed molecule in the preparation of the nD/NaLZ-105 systems essentially inhib-

Table 1. Terminal Selectivity and Dichloride Product Distribution of the Chlorination of Dodecane and 1-Chlorododecane in LZ-105 Zeolites^a

zeolite	loading (wt %)	S_i^b	1,1DCD ^c (%)	1,2DCD ^d (%)	1,12DCD ^e (%)	R^f
<i>n</i> -Dodecane ^g						
LiLZ-105	4	7.8	40	30	19	0.27
NaLZ-105	4	8.3	34	34	12	0.18
KLZ-105	4	11.2	36	34	17	0.24
RbLZ-105	4	9.1	33	33	18	0.27
CsLZ-105	4	5.7	28	43	13	0.18
1-Chlorododecane ^h						
NaLZ-105	3	8.1	13	4.7	49	2.8

^a Error units in yields estimated to be ca. 10% of the indicated values.

^b For dodecane as substrate, $S_i = (\% \text{ yield of 1-chlorododecane}/3)/(\% \text{ yield of other monochlorododecane}/10)$. For 1-chlorododecane as substrate, $S_i = (\% \text{ yield of 1,12-dichlorododecane}/3)/(\% \text{ yield of other dichlorododecane}/22)$. ^c 1,1DCD, 1,1-dichlorododecane. ^d 1,2DCD, 1,2-dichlorododecane. ^e 1,12DCD, 1,12-dichlorododecane. ^f $R = \% \text{ yield of 1,12-dichlorododecane}/(\% \text{ yield of 1,1-dichlorododecane} + \% \text{ yield of 1,2-dichlorododecane})$. ^g Low yields (5–15%) of 1,3-dichlorododecane were also formed. ^h Low yields (ca. 3%) of 1,3-dichlorododecane were also formed.

ited all photochlorination. Although the use of benzene as a coadsorbed molecule in the preparation of the nD/NaLZ-105 systems reduced the extent of photochlorination considerably, it did not completely shut down the reaction, as was the case with pyridine as coadsorbant. The value of S_i dropped from ca. 8 to 4.3 on addition of benzene.

Effect of Compensating Cation on the Selectivity of Dichlorination in the Photochlorination of nD *in Situ*. The distribution of dichlorides produced in the photochlorination of nD *in situ* was investigated for a series of LZ-105 zeolites possessing various metal cations (MLZ-105). In general, for the systems investigated, the dichlorination products make up 10–20% of the converted nD in the photochlorinations performed on nD/MLZ-105. For example, for NaLZ-105, at 4% loading of nD, 1,1DCD (Figure 2e) and 1,2DCD (Figure 2f) are the major products (ca. 60% of the dichlorinated products), 1,12DCD (Figure 2h) is a minor product (ca. 18% of the dichlorinated products), and 1,3DCD (Figure 2g) is a trace product (ca. 5% of the dichlorinated products).

The effect of a compensating metal cation on the dichloride product distribution produced from the dichlorination of nD is given in Table 1. The smaller cations (Li, Na, and K) favor the formation of 1,1DCD slightly and the yield of 1,12DCD is relatively insensitive to the cation. For HLZ-105, the yield of 1,2DCD in the product distribution is significantly higher than in the case of the metal cations. Similar results were observed for silicalite.

Comparison of the Products of the Second *in Situ* Chlorination of nD and the First Chlorination of 1CD. The relative yields of the 1,nDCDs produced by the monochlorination of 1CD and the dichlorination of nD differ substantially (compare parts C and F of Figure 2) for the NaLZ-105 systems. For the *in situ* dichlorination of nD the major products are 1,1DCD and 1,2DCD, with 1,3DCD and 1,12DCD as minor products. The major products in the monochlorination of 1CD are 1,12DCD and 1,1DCD with the remaining 1,nDCDs as minor products (Figure 2F). Furthermore, the ratios of yields of 1,1DCD and 1,2DCD produced by the two methods differ substantially. For example, the ratio of 1,1DCD/1,2DCD (major products) produced from *in situ* dichlorination of nD adsorbed on NaLZ-105 is ca. 1 (Figure 2C), whereas the ratio of 1,1DCD/1,2DCD (minor products) produced from the monochlorination of 1CD adsorbed on NaLZ-105 is ca. 2.8 (Figure 2F).

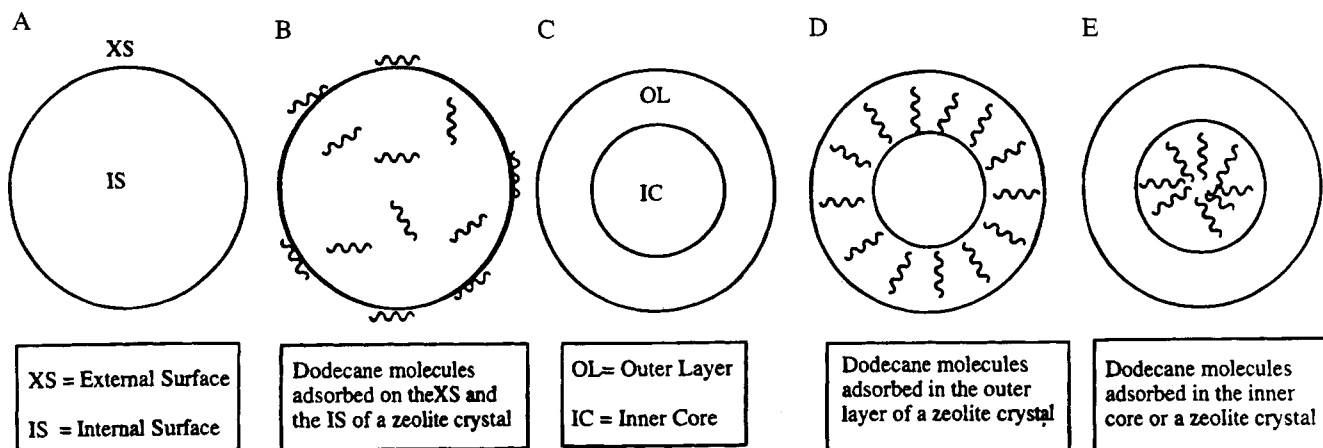
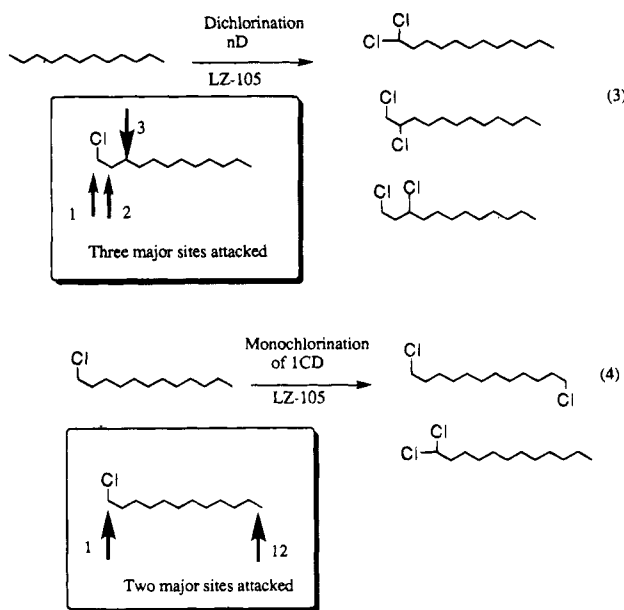


Figure 5. Schematic representations of the structure of a pentasil crystal, which is treated as a topological sphere containing a second, smaller topological sphere. This description allows for a classification of the qualitative siting of substrate molecules.

Discussion

Salient Features of the Product Distributions That Require Mechanistic Interpretation. We seek to generate a supramolecular model that incorporates dynamic features of diffusion of reagents and provides a plausible working paradigm to explain the following salient features of the results: (1) the mechanistic basis for the high terminal selectivity for pentasils containing alkali cations (LZ-105) compared to silicalite and the H form of LZ-105; (2) the mechanistic basis for the variation of S_t , S_i , and S_m with reaction conditions in the monochlorination of nD; and (3) the mechanistic basis for the differences in the product profiles in the *in situ* dichlorination of nD and in the monochlorination of 1CD.

The salient results are summarized in eq 1 (above) and eqs 3 and 4.



Generation of a Model for the Supramolecular Structures for Adsorption of nD and 1CD Molecules on Pentasil Zeolites. Topological Considerations. To analyze the results, we shall generate a supramolecular structural model that is consistent with the known internal and external surface structure of the host pentasil zeolite systems and the molecular structure of the guests nD and 1CD. First, we consider the host's external and internal surface structure. Consider a representation (qualitative restricted space) of a single crystal of a pentasil

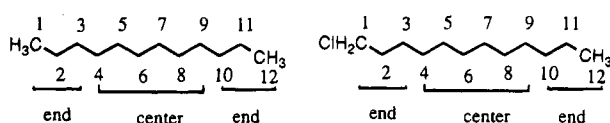
zeolite (Figure 5) as a *topological object* possessing an outside, a boundary, and an inside. We assume that there are two plausible *topological* locations for the adsorption of nD (or 1CD) molecules (Figure 5A): (1) the **external surface** (XS, the "air"/solid interface) of the crystal and (2) the **internal surface** (IS) of the crystal that is accessible to nD. All of the results in this paper will refer, unless noted otherwise, to nD molecules or 1CD molecules adsorbed on the IS, i.e., to photochlorinations performed at low enough coverage so that the vast majority of guest molecules resides on the internal surface.

For example, we term a pentasil crystal containing nD molecules adsorbed on the XS or IS a *global supramolecular structure*, nD/Z. We seek to describe the *local supramolecular components* that make up the crystal nD/Z in structural terms that are analogous to those that have proven so effective for description of molecular systems. First, we recognize that for an individual crystal, nD/Z, some of the adsorbed molecules (whatever their orientation in the L, I, or Z sites) are closer to the external surface of the crystal than others. Thus, we may also consider the IS as a restricted space which itself consists of two topological regions of potentially differing reactivity (Figure 5C,D,E): a region of the IS space consisting of an **outer layer** (OL) of the nD molecules that happen to be closest to the external surface and a region of the IS space consisting of an **inner core** (IC) comprising all of the remaining nD molecules that are not in the OL. The importance of these structural distinctions results from the expectation that the inherently high reactivity of the reagents ($\text{Cl}_2/\text{Cl}^\bullet$) in the chlorination with nD will tend to make the chlorination reaction diffusion- and/or collision-controlled and therefore dependent on the *molecular traffic control*⁷ of the reagents percolating into and through the internal surface. Under the assumption of diffusional and collisional control of reactivity, molecules located closest to the external surface (i.e., in the OL) will possess an enhanced reactivity simply *because of their proximity to the external surface*. In addition, the molecules in the OL exert a *supramolecular steric effect* on molecules in the IC that are less reactive because reagents are inhibited from diffusing through the OL.

In addition, these global topological features (XS, IS, OL, and IC) of a nD/Z crystal are pertinent to the observation that pentasil crystals are often found to possess an Al distribution that is nonuniform, with a higher concentration of Al in the outer layer of the crystals.¹¹ Thus, the results may be influenced by the uniformity or nonuniformity of the distribution of Al

(11) von Ballmoos, R.; Meirer, W. M. *Nature* **1981**, 289, 782. Lin, J. C.; Chao, K. J. *J. Chem. Soc., Faraday Trans. 1* **1986**, 82, 2645. Chao, K. J.; Chern, J. Y. *Zeolites* **1988**, 8, 82.

Scheme 1



sites in the case of LZ-105 as a host. Pentasil crystals employed to determine the Al distributions are grown using tetrapropylammonium ions as templates, because this approach can yield crystals large enough for the Al distribution analysis. However, we note that the LZ-105 crystals employed in this investigation are grown using seeding techniques.¹²

Generation of a Model for the Supramolecular Structures for Adsorption of nD and 1CD Molecules on Pentasil Zeolites. Geometric and Chemical Features. Supramolecular Geometric Isomers. Since the X-ray structures² of silicalite and ZSM-5 are equivalent to those for the pentasil LZ-105,¹² the void space geometry shown in Figure 1 refers to silicalite, ZSM-5, and LZ-105. Thus, the *geometric representation* (quantitative dimensions and shapes) and the connectivity relations of the internal *void space* of these zeolites are known with great accuracy and confidence. In Figure 1 the three distinct types of void spaces that can serve as sites for adsorption of nD or 1CD (maximum extended length in the all-trans configuration ca. 17 Å) along with the dimensions of the void spaces are shown: (1) the zigzag channel (Z, ca. 6.7 Å in length); (2) the linear channel (L, ca. 4.5 Å in length); and (3) the intersection of the Z and L channels (I, ca. 5.4 Å in length). From these considerations, we note that *only certain connectivity relations are possible for guest molecules sited on the internal surface*. It is also important to note that the (roughly spherical) I site is relatively large (effective space of ca. 9 Å along the diagonal) compared to the L and Z sites, a structural feature that is not immediately apparent from Figure 1.

Since only certain connected combinations of the void space components L, I, and Z can accommodate an nD or a 1CD molecule, we need to examine the structure of these guest substrates in terms of plausible "pieces" that can "fit" into the various possible connected void space sites (Scheme 1). For example, it is convenient to consider the guest conceptually in terms of the ends and the center of the molecule, each of which is roughly the "length" (ca. 5–6 Å) of one of the void space components. We define an **end** of an nD molecule as the terminal methyl groups (carbon 1 or 12) and the next two connected pairs of "peripheral" methylene groups (carbons 2 and 3 or 10 and 11). We define the **center** of an nD molecule as the remaining methylene groups (carbons 4–9).

The convenience of this classification will be seen to reside in its ability to allow for identification of the portions of the nD molecule that can fit in the various possible connected L, I, and Z sites and to provide a language to describe and to classify the supramolecular structures that are *plausible* for describing the supramolecular structure of a pentasil crystal containing nD. For example, an end (length ca. 5 Å) or the center (length ca. 7 Å) of nD can fit readily into a Z site (length ca. 6.7 Å), but only two or three carbon atoms (length ca. 5 Å) can fit into an L site (length ca. 4.5 Å). About three carbon atoms in a trans form can fit into the L site (length along the channel axis ca. 5 Å), but more than three carbon atoms can fit into an I site (length diagonal to the channel axis ca. 9 Å) if gauche forms occur. This

classification allows a convenient supramolecular structure basis for the analysis of the terminal selectivity data (S_t , selectivity of the terminal methyl attack to the methylene attack) and secondary selectivity data (S_i , selectivity of the attack of internal methylenes to central methylenes).

Figure 6 shows a computer-generated representation¹³ of an nD molecule sited in a linear channel of a pentasil zeolite. The kinetic diameter of a linear *n*-alkane is ca. 4.3 Å. Since the linear channel possesses an elliptical shape of ca. 5.1 × 5.7 Å, there is insufficient space in an occupied site for a chlorine reagent (effective diameter ca. 2 Å) diffusing down a linear channel to maneuver past the first methyl group bound in an L site to attack the adjacent methylene group. In addition, for the hydrogen on the 2-carbon to achieve a reasonable conformation for reaction with the chlorine, the nD molecule would have to distort so that the terminal methyl group would be forced into the channel wall, which is expected to be a high-energy structure.

Definition of the Plausible Local Supramolecular Structure of an nD/Z System. We now consider in detail all of the **plausible supramolecular local component structures** of nD/Z that can exist within the crystal (in either the OS or IC region) in terms of the occupancy of **three** contiguous or connected sites (which can accommodate an nD molecule) and are available within the internal surface. A set of three connected (Z, I, and L) sites is termed a **void space host constitution** in the same sense that a set of connected atoms represents a molecular constitution. For example, at least six plausible host constitutions that can accommodate an nD molecule (Figure 7) can be envisioned on the basis of simple commensurate length considerations of the guest and host constitutions: LIL, LIZ, IZI, IZL, ZIZ, and ZIL. Other possible host constitutions (LLL and ZLZ) are implausible (realistically impossible) from simple connectivity considerations. For example, each nD molecule (length ca. 17 Å in the all-trans form) can span ca. three connected host sites. The important result of these structural considerations is that *we need only consider six plausible supramolecular structures in the analysis of the results*: LIL (16 Å), LIZ (18 Å), ZIL (18 Å), ZIZ (20 Å), ILI (17 Å), and IZI (17 Å), where the approximate dimensions in parentheses are the lengths of the three contiguous sites.

The various nD/Z systems formed by occupancy of the six void space constitutions can be considered as **isomeric supramolecular structures if they do not interconvert during the time scale of the photochlorination**. In this case each supramolecular isomer can be considered a distinct chemical species having measurably different reactivities in the chlorination reaction. We will refer to these supramolecular constitutional isomers simply as **structural isomers** of the nD/Z crystal. These structural isomers may, in turn, be classified in terms of their geometric and stereochemical characteristics.

Generation of a Model for the Supramolecular Structures for Adsorption of nD and 1CD Molecules on Pentasil Zeolites. Regiochemical and Stereochemical Aspects. Supramolecular Regioisomers and Supramolecular Stereoisomers. Examination of the details of the local supramolecular structures of nD/Z also reveal **both a regiochemical and a stereochemical** aspect. Specifically, four of the six supramolecular isomers described above (Figure 7) possess one end of the nD molecule within the structure that is closest or **proximal** to the external surface of the crystal and a second end that is further away or **distal** to the external surface of the crystal. The two exceptions are the IZI and ZIZ isomers for which the two ends of the nD molecule are equivalently positioned with respect to the distance from the external surface. Thus, for these two

(12) Grose, R. W.; Flanigen, E. M. U.S. Pat. 4,257,885, issued March 24, 1981.

(13) The computer simulations were performed with ChemX software, developed by Chemical Design Ltd., Oxford, England. See: Ramas, S.; Thomas, J. M.; Betteridge, P. W.; Cheetham, A. K.; Davies, E. K. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 671.

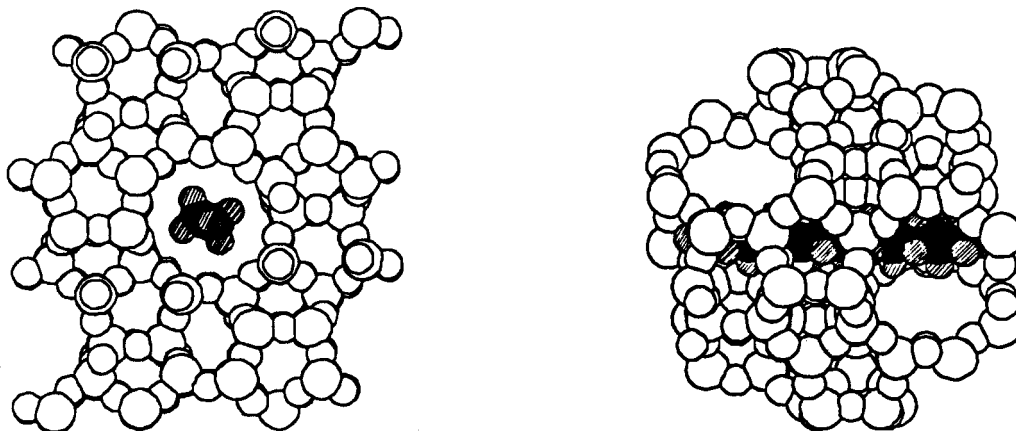


Figure 6. (Left) Computer representation of an axis view of an *n*-dodecane molecule adsorbed in the linear channel of a pentasil zeolite. (Right) Computer simulation of a side view of an *n*-dodecane molecule adsorbed in the linear channel of a pentasil zeolite. Atoms are drawn at their covalent radii (CPK model). Note that the exposed "end" of the *n*-dodecane molecule on the left is viewed through the zigzag channel.

isomers the proximal/distal relationship does not apply (compare the term meso for diastereomers). These considerations reveal a regiochemical aspect of the local nD/Z systems resulting from the formation of the supramolecular guest–host complex and that does not exist for the guest when considered only in molecular terms in the absence of the host. Therefore, we need to describe this regiochemical aspect in terms of the L, I, and Z terminology.

Consider, for example, an LIZ supramolecular isomer for which the L group is proximal and the Z site is distal. We could label this isomer *pLIdZ* (*p* for proximal and *d* for distal). However, a simpler and unambiguous nomenclature is available, if we simply accept the convention that for those isomers displaying regiochemical features, the first letter in the designation will refer to the proximal position and the last to the distal position. As a result of this regiochemical attribute, for an LIL supramolecular isomer, the proximal position (left L by convention) is expected to be more reactive than the distal position (right L by convention). Thus, two terminal methyl groups of a linear alkane, which are expected to possess exactly equivalent reactivity in molecular terminology, are expected to have potentially very different reactivity in supramolecular terminology.

If required, the outer layer or inner core aspect of the supramolecular isomers is denoted by adding (OL) or (IC) to the isomer designation, i.e., LIZ(OL) and LIZ(IC) refer to dodecane molecules in the LIZ sites in the outer layer and in the inner core, respectively. We shall see that the results apply mainly to guest molecules located in the OL, so unless stated explicitly to the contrary, all further discussion will refer to supramolecular isomers in the OL only.

If the ends of a guest molecule, such as 1CD, are chemically distinct, a further possibility exists that each of the structural isomers (except the "stereochemically silent" ZIZ and IZI isomers) will exist as **supramolecular stereoisomers**. In this case, the addition of Cl at the left (proximal) or right (distal) position of the isomer designation allows an unambiguous nomenclature; i.e., CILIZ means that the chlorine atom is proximal. The outer layer and inner core designations follow from the above example. Thus, LIL(OL) isomers are expected to be more reactive than LIL(IC) isomers because of the steric or blocking effect of the guest molecules in the OL. Furthermore, for the two stereoisomers, LILCl and CILIL, the former is expected to be more reactive because the methyl group is proximal; i.e., the proximal ClCH₂ group is less reactive because of the steric effect of the Cl atom.

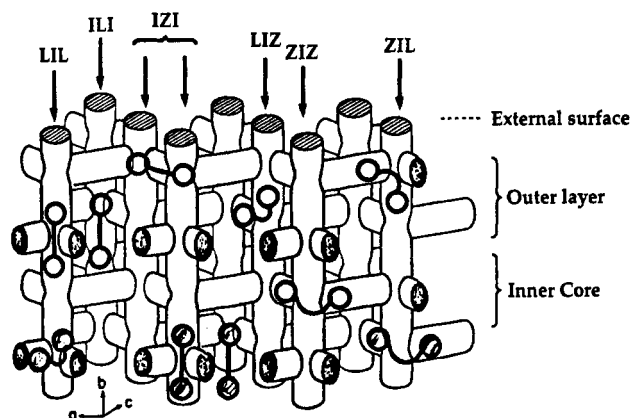


Figure 7. Schematic representation of the plausible sitings of *n*-dodecane in the void space of the internal surface of a pentasil zeolite. See text for discussion.

In summary, an individual nD molecule adsorbed on the internal surface may be classified (1) *topologically*, in terms of its location in the outer layer or in the inner core; (2) *regiochemically*, in terms of its supramolecular constitutional structure or structural isomerization indicating the three void space sites spanned by the molecule; and (3) *stereochemically*, in terms of guest orientation relative to the external surface. Although it is quite difficult to determine the details of the distribution of configurations of *n*-alkanes in the internal framework as a function of coverage or cations and other variables, in the remainder of the discussion we attempt to employ the supramolecular structural model presented above as a structure–reactivity linkage between the isomer distributions of the nD/Z crystal and the distribution of products of photochlorination.

Development of a Working Paradigm for Photodichlorination of Linear Alkanes Adsorbed on Pentasil Zeolites. On the basis of information from the literature of photochlorination¹⁴ and the structural parameters of the zeolite host² and the nD and 1CD guests, photochlorination is envisioned as occurring as follows. It is assumed that the major source of chlorine atoms and chlorine molecules (reagents) is external to the zeolite crystal (XS) and that the reagents enter the zeolite crystal

(14) (a) For a general review of photochlorination see: Huyser, E. *Advances in Free Radical Chemistry*; William, G. H., Ed.; Logos: London, 1965; Vol. 1, p 79. Russell, G. A. *Tetrahedron* **1960**, *8*, 101. (b) For attempts to achieve selectivity by adsorption on substrates see: Perry, E. *J. Org. Chem.* **1970**, *35*, 2053. Eden, C.; Shaked, Z. *Isr. J. Chem.* **1975**, *13*, 1.

through the windows on the air/external surface interface. The assumption that the reagent is generated externally to the zeolite crystal is supported by the lack of sensitivity of the product distribution and rate of conversion to the charge of chlorine employed in the experiments.

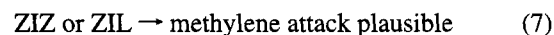
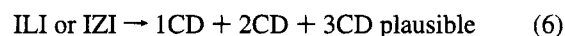
From consideration of the details of the crystal packing and crystal structure of pentasils, the reagents may enter the crystal² through either the windows on the air/external surface interface leading to a linear channel (the 010 face of a well-formed crystal) or through the windows on the air/external surface interface leading to a zigzag channel (the 100 or 001 face of a well-formed crystal). Since the tortuosity of the zigzag channels is 4 times that of the linear channels, it is expected that the reagents will preferentially and more rapidly diffuse along the linear channels.¹⁵ This conclusion is supported by both experimental^{8,16} and computational⁶ results which conclude that the diffusion of small molecules occurs preferentially along the linear channels. Thus, we assume for a working model for the photochlorination of nD/Z that the reagents entering the internal void space prefer to diffuse along the linear channels and that diffusion through the zigzag channel is significantly slower.

After entering the internal void space through the air/external surface interface, the reagents diffusing through linear channels eventually encounter the isomeric supramolecular structures residing in the outer layer of an nD/Z particle (Figure 7). Because of the high reactivity of the reagents, the monochlorination product distribution is expected to be determined by the probability of collisions that the diffusing reagents make with the proximal ends or proximal centers of the nD molecules that are distributed in the outer layer. From this point of view, if a diffusion path along the linear channels is followed, the proximal groups in the linear channels (either the ends or the center of the nD molecule) should be attacked preferentially. Thus, the model predicts that the favored products of monochlorination should be a function of the distribution of the isomeric structures in the outer layer, if the nD molecules do not rapidly exchange their positions during the time scale of the experiment (minutes).

That the isomeric supramolecular structures do not rapidly equilibrate is supported both by literature data on the binding affinities and rates of diffusion of *n*-alkanes in pentasil zeolites^{16,17} and by experimental observations that the photochlorinations cannot be run to high conversions and that dichlorination occurs rapidly at relatively low conversions. If rapid equilibration of the supramolecular isomers occurred, high conversion of all of the nD molecules to chlorinated products would be plausible. The conclusion of nonequilibration of isomeric supramolecular structures is further supported by the insensitivity of S_t and S_m to temperature ($S_t = 7.3$ at 24 °C and 8.4 at 73 °C; $S_m = 81\%$ at 24 °C and 73% at 73 °C), since at higher temperature more rapid equilibration would be encouraged.

If a proximal end of an nD molecule is in an L site (LIL or LIZ, Figure 7), the only monochlorination product expected to be formed by reagent attack through the linear channel is 1CD, since there is not enough space for a reagent to move into the linear channel past a carbon atom (Figure 6). Therefore, we conclude that for the LIL or LIZ structure only terminal

chlorination is plausible (eq 5). However, if an end of an nD molecule is located at an intersection, there is probably enough room for attack of the chlorine reagents at each of the 1-, 2-, and 3-carbons; we further conclude that for the ILI structures monochlorination at the 1-, 2-, and 3-positions is plausible (eq 6). Finally, if the center of an nD molecule is located at an intersection, the reagent attack will be on the internal methylene groups (eq 7)

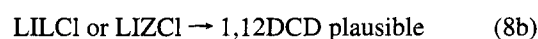


Furthermore, the rate of dichlorination from attack by later waves of reagents along the linear channels is expected to be very slow because of the steric blocking by the Cl atom at the proximal position in an L site. However, dichlorination could result if the siting shifts slightly from LIL and LIZ (i.e., a jump of one carbon atom) to one in which the proximal end moves to an intersection (i.e., to ILI or IZI). Such small displacements to adjacent sites are not inconsistent with the known diffusional motion of *n*-alkanes in ZSM-5 zeolites.¹⁷ If such structural reorganization occurs, the second chlorination could occur again at the proximal end to produce 1,nDCD ($n = 1, 2$, or possibly 3), because there is enough room (ca. 9 Å along the diagonal) in the intersection to accommodate a $-\text{CH}_2\text{Cl}$ group and a reagent Cl atom. The formation of 1,1- and 1,2DCDs as the major dichlorinated products and the near absence of formation of n,mDCDs without a chlorine on the 1-position are consistent with this being the major mechanism for the formation of DCDs. Thus, it appears that relatively rapid but structurally minor interconversions of supramolecular isomers between adjacent contiguous sites might be possible, although (see above) rapid massive equilibration of supramolecular isomers is ruled out.

If a proximal end of an nD molecule is in an intersection (ILI or IZI), it is expected that 1- or 2CDs would be produced as the major products from reagent attack through the linear channels (with 3CD as a possible minor product). In the case of the IZI configuration, some 1,12DCD is also expected to be produced by waves of reagents which follow the first chlorination.

In the cases of the ZIZ and ZIL configurations, reagent attack through the linear channels will result in chlorination of the center methylene groups (which are proximal and located in the I sites) to produce nCD ($n = 3-6$). Dichlorination of the monochlorinated product produced from these supramolecular isomers would produce m,nDCDs ($m \neq 1$); however, this possibility is not plausible both because the Cl atom will tend to lock the nCD molecule into the precursor configuration and because the Cl atom will serve to block further chlorination sterically in its vicinity. Indeed, there is no evidence for the importance of such reactions since m,nDCDs are not produced in significant yields.

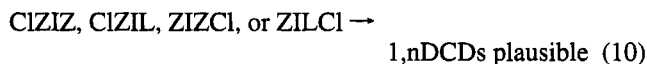
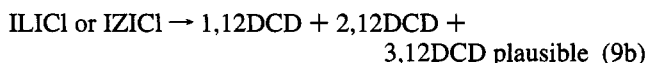
Development of a Working Paradigm for Photochlorination of 1CD Adsorbed on Pentasil Zeolites. Given the above analysis we can now proceed to enumerate economically the expected results of the photochlorination 1CD/Z. In this case the number of supramolecular isomers must include the stereoisomers resulting from the asymmetry of the 1CD molecule. The plausible products are listed in eqs 8-10.



(15) Geus, E. R.; den Exter, M. J.; van Bekkum, H. J. *Chem. Soc., Faraday Trans.* **1992**, *88*, 3101; quoting Hong, U., et al. *Zeolites* **1991**, *11*, 816.

(16) Hayhurst, D. T.; Paravar, A. R. *Zeolites* **1988**, *8*, 27.

(17) Haag, W. O.; Lago, R. M.; Weisz, P. B. *Faraday Discuss. Chem. Soc.* **1981**, *72*, 317. (b) Derouane, E. G. In *Zeolites: Science and Technology*; Ribeiro, F. R., et al., Eds.; Nijhoff: Boston, MA, 1984. (c) Rathven, D. M. In *Principles of Adsorption and Adsorption Processes*; Wiley: New York, 1984.



Interpretation of the Results within the Working Model. Effect of Loading on the Selectivity of Terminal Chlorination of nD. One of the most salient observations of this investigation is that, independent of the cation, the selectivity for terminal chlorination, S_t , reaches a maximum in the range of ca. 4% loading (corresponding to ca. 50% coverage of the internal surface). The reason for the maximum in terminal selectivity might be explained plausibly in terms of the working model in several ways. First, there might be a **dynamic mechanism** which could reduce selectivity; i.e., at low loading there might be an interchange of nD molecules between the outer layer and the inner core during the time scale of the experiment (leading to both rapid outer layer/inner core and massive supramolecular isomerization). We rule out this mechanism because, if it were correct, complete and/or high conversions would be possible at lower loadings and more polychlorination would be found at lower loadings. In addition, it is implausible that equilibration would occur at low loadings and high loadings but not at intermediate loadings. Therefore, we conclude that the nD molecules do not equilibrate during the experimental time scale at either the high or low loading investigated. However, at low loading the reagents may diffuse more randomly and be able to percolate through the zigzag channels in addition to the linear channels.

A second possibility is a **topological structural mechanism** for which, at low loading, some nD is adsorbed externally (XS in Figure 5) and this material is photochlorinated more rapidly and less selectively than internally adsorbed nD (IS in Figure 5). If the contribution of the externally photochlorinated products is greater at low loadings for some unanticipated reason, the overall selectivity will be less than that at higher loadings where the net contribution from photochlorination from nD adsorbed on the internal surface is larger and the selectivity will be increased. This possibility is ruled out as implausible on the basis of the observed profile of structures of the DCDs produced; i.e., the same profile is formed from the dichlorination of nD *in situ* and from the monochlorination of 1CD (although the ratios are different). If photochlorination occurred on the external surface, significant formation of m,nDCDs ($m \neq 1$) is expected but is not observed. Furthermore, it was found that samples initially loaded with 10–20% of nD adsorbed on NaLZ-105, where some nD must be on the XS, generated many other DCDs in addition to the 1,n-DCDs, and so we conclude that significant photochlorination of nD adsorbed on the external surface does not occur for loadings of the order of ca. 4%.

A final possibility is a **thermodynamic supramolecular structural redistribution mechanism** for which, at low loadings, the distributions of configurations of the intracrystalline isomeric supramolecular structures in the nD/zeolite complex are relatively random (i.e., all six supramolecular isomers in Figure 7 are comparably populated). The results would be explained by this mechanism if, as the loading is increased, the distribution of the isomeric mixture changes in a manner to favor those isomers leading preferentially to terminal chlorination, e.g., if at higher loadings supramolecular isomers such as the LIL and LIZ isomers were favored. In the latter case, the preponderant isomers would place methyl groups in a proximal position in the linear channels and favor formation of the terminally chlorinated products. We conclude that this mechanism is consistent with all of the reported observations and is intuitively

reasonable because adsorption in the L or Z sites maximizes the dispersive and van der Waals interactions that are believed to be important interactions in the binding of linear alkanes to the framework atoms.⁶

There is a certain amount of information in the literature that is relevant to the issue of how *n*-alkane/zeolite supramolecular structures, such as those of nD/ZSM-5, rearrange as a function of loading.^{8,16} This is an important concern for catalysis since it addresses the issues of number and occupancy of active sites as a function of loading. An early study of the adsorption of nD on ZSM-5 led to the conclusion that at maximum coverage even the zigzag channels were occupied.⁸ These conclusions were reached on the basis of the amount of nD at maximum attainable loading and the observation that the internal surface was computed to be only about 60% covered and that this value for coverage of the internal surface is close to that expected for complete coverage of the zigzag channels alone. If these results are correctly interpreted, from our working model the concentration of structures LIZ and LIL rises to a maximum at a 4% loading and then decreases in population from that at which maximum S_t is obtained. The other structures (IZI, ILI, ZIL, and ZIZ) would be populated to a greater extent as the maximum coverage of the internal surface is approached. Simultaneously, pathways that could lead to reaction of molecules in the IC would become more inhibited (Figure 5).

We point out, however, that it is not clear whether it is safe to extrapolate the work dealing with adsorption of linear hydrocarbons on ZSM-5 as a basis to understand our systems, because ZSM-5 in the reported systems was synthesized using tetrapropylammonium ions as templates, while LZ-105 employed in our investigations is grown without an organic template and uses pentasil crystals as seeds.¹² More importantly, the literature adsorption studies were performed on HZSM-5, which gave poor selectivity in our work. Since it was noted⁸ that going from HZSM-5 to NaZSM-5 drastically changed the absorption isotherms for nitrogen, the role of cations is clearly important. Finally, the assumption that at 60% coverage only the Z sites are occupied is speculative and does not appear to have been confirmed by more definitive evidence.

Effect of Varying Cation on the Selectivity of Terminal Chlorination of nD. Although the relative number of Al atoms making up the framework of pentasil zeolites is small compared to the number of Si atoms, the Al atoms are critical for the catalytic characteristics of zeolites.¹⁸ The Al atoms cannot be accurately located in the framework by X-ray crystallography because of the similarity of the electron distribution of the Al and Si atoms. However, it is generally assumed that the catalytically active cations (usually protons) associated with Al atoms are located near the Al framework atoms (to maintain electrical neutrality) as the result of attractive Coulombic forces. A challenge in the current paper is to employ the results of chlorination to deduce the location of the cations in the pentasil framework and therefore to establish the location of both the active sites and the Al atoms.

In the photochlorination of nD adsorbed on silicalite (no cations), the terminal selectivity is the lowest observed (S_t ca. 2) and is comparable to that for HLZ-105 (smallest cation). The general increase in S_t when alkali cations are added to the system is attributed to a distribution of internal surface supramolecular isomers that are cation-dependent. This result is consistent with the intuitive notion that the distribution of supramolecular isomers contained in the internal surface will depend on the existence of other species (cations and other guest molecules

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such as benzene and pyridine) that may or may not be mobile and that compete for space in the internal surface. It is also consistent with the experimental observations that the maximum loading of *n*-alkanes adsorbed on ZSM-5 zeolites is dependent on the nature of the compensating cation⁸ and that the space accessible to adsorbants is dependent on the number density and nature of the cations.¹⁹

For an nD/silicalite crystal at ca. 4% loading the distribution of nD molecules on the internal surface is unobstructed by cations. For the nD/HLZ-105 particle at ca. 4% loading the distribution of nD molecules is minimally obstructed by the small H cations. The photochlorination of the nD/silicalite and HLZ-105 particles is relatively unselective and results in comparable yields of 1-, 2-, and 3CD and 4-, 5-, and 6CD. Since 1CD is a major product expected from reagents attacking nD molecules in the LIL and LIZ configurations (eq 5), since 2- and 3CD are major products expected from reagents attacking nD molecules in the ILI and IZI configurations (eq 6), and since 4-, 5-, and 6CD are major products expected from reagents attacking nD molecules in the ZIZ and ZIL configurations (eq 7), we conclude that *essentially all of the possible configurations of the nD/silicalite complexes are comparably populated*. This result is compatible with the hypothesis that a random distribution of isomers leads to nonselective photochlorination and that the absence of cations or the occurrence of small cations is favorable for a random distribution.

The result for silicalite is also consistent with the idea that for NaLZ-105 the Si-rich regions of the crystals are occupied first when nD molecules are loaded. Regions that are Si-rich are also cation-poor and therefore resemble silicalite. Thus, the values of S_i for low loading of NaLZ-105 should be similar to those on silicalite at any loading if distributions, and not reagent dynamics, are the dominating factor in determining product distributions. Evidence has been provided²⁰ that smaller alkanes preferentially occupy zigzag channels in silicalite first. Following this logic, we expect that at higher loadings the nD molecules are eventually forced to occupy Al-rich and cation-rich regions. We propose that the occurrence of the cations, which are expected to be sited near the intersections (but not necessarily in the intersections),³ will cause a redistribution of the population of structural nD/Z isomers that react preferentially to yield terminal chlorination. Thus, the product distribution contains information on the distribution of isomers.

The working mechanism developed so far suggests that all compensating alkali cations cause an increase in the value of S_i compared to silicalite. Compensating cations on the internal surface of LZ-105 zeolites are generally believed to be located near the channel intersections where the quaternary ammonium template cations reside. From the Si/Al ratio of 20 for LZ-105, it can be speculated that each intersection may possess one or two compensating cations. Since the terminal selectivity increases in the presence of compensating cations, we propose that the role of the cation is to cause a redistribution (compared to silicalite) of the nD/Z isomers to favor the LIL and LIZ configurations, which are expected to favor formation of 1CD. Hence, the variation in selectivity with cations is considered to be the result of supramolecular isomer distributions that change as a function of cation structure and location; i.e., **the cations located in the Z sites will steer the ZIZ, ZIL, LIZ, and IZI population toward the LIL isomer by pushing the nD**

molecules out of the Z sites and thereby steer the selectivity of the photochlorination toward the terminal chlorination (eq 5).

This mechanism is further supported by the observation of a marked increase in S_i for the largest cations. In structural terms, this observation indicates a dramatic decrease in the ZIZ and ZIL configurations for these cations. Both this result and the variation of S_i with cation suggest that the larger cations limit access to the Z sites.

Theoretical Effect of Loading on Selectivity of Dichlorination of nD Based on the Working Model. On the basis of the working model (no rapid exchange of substrate molecules from their initial sites during the reaction diffusion of reagents down the linear channels)¹⁶, at higher conversions the chlorination of nD will become more difficult, since the nCD in the OL formed by the first chlorination will tend to form a steric barrier for diffusion of reagents through the linear channels (Figure 5). As a result, the reagents must seek tortuous routes to find nD molecules located in the IC. Thus, after chlorination of the outer "monolayer" of nD in the OL, the rate of conversion is expected to slow down significantly. At this point, **dichlorination** of the nCD molecules formed in the OL might occur more rapidly than the monochlorination of the sterically "blocked" nD molecules in the IC layer. The first chlorination may also have the effect of "locking" a CD molecule at the site at which it was created for the remainder of the chlorination, both because of an electrostatic interaction of the CD with nearby cations and because of the expected slower diffusion or site jumping resulting from the larger size of the Cl atom.

The net result is that the major dichlorination products result from the same factors that produced the major monochlorination products: the distribution of the sitings and diffusion of the reagents in the linear channels. Thus, dichlorination of the end carbon atoms is expected to be strongly favored, i.e., 1,1DCD from 1CD and 1,2DCD from 1CD, which exists as CILIL or CIILI supramolecular isomers.

Experimental Selectivity in the Monochlorination of 1CD.

As discussed above, the sitings of 1CD present a stereochemical aspect that is absent for nD: since the ends of the 1CD molecule are distinguishable, two stereoisomers of the same constitutional (LIZ) isomers become possible, with the exception of the ZIZ and IZI isomers for which the proximal and distal positions are stereochemically equivalent. For the remaining supramolecular isomers capable of stereoisomerization, the terminal CH₂Cl group may be either proximal or distal. From the results and conclusions for the *monochlorination* of nD, the major products expected for proximal chlorination of 1CD are 1,1DCD and 1,2DCD, if the 1CD is oriented with its CH₂Cl group proximal and in an L or I site (eqs 8a and 9a), and 1,12DCD, if the 1CD is oriented with its CH₂Cl group distal and in an L or I site (eq 8b). The possibility of significant contributions from ILICl or IZICl isomers is ruled out by the lack of formation of the expected products (eq 9b), as is the possibility of significant contributions of CIZIZ, CIZIL, ZIZCl, or ZILCl isomers (eq 10). Thus, we need only consider contributions from the supramolecular isomeric structures shown in eqs 8a, 8b, and 9a.

Since 1,1DCD and 1,12DCD are the major products formed from the photochlorination of 1CD adsorbed onto LZ-105, we conclude that *only the isomers represented by eqs 8a and 8b (CILIL, CILIZ, LILCl, and LIZCl) are required to explain the major results of this investigation*. However, since the 1-position may possess a lower reactivity relative to the 12-position, it is not clear whether the product distribution can be as definitively related to the supramolecular isomer distribution

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as was the case for nD. Indeed, if the solution results^{10,14} concerning the selectivity of chlorination of alkanes are considered, it is concluded that the relative fraction of the proximal and distal geometrical isomers may be comparable. From these considerations, the percentage of proximal and distal CH₂Cl groups of the 1CD/Z complex would be considered to be comparable.

The possibility that initial attachment of the Cl at the distal position to the zeolite surface may be preferred is consistent with the observation that, from an equal molar mixture of 1CD and nD, 1CD is absorbed more rapidly than nD into the internal surface of LZ-105.

The formation of trace products (1,nDCDs, $n = 2-11$) is consistent with a small amount of monochlorination of 1CD at the ILI and IZI sitings (eq 9b) or at the ZIZ and ZIL sitings (eq 10).

Comparison of the Products of the Second Chlorination of nD and the First Chlorination of 1CD. The same DCDs are produced from the dichlorination of nD *in situ* and from the monochlorination of CD. Since all DCDs produced from monochlorination of 1CD must be 1,nDCDs, all DCDs produced from the dichlorination of nD *in situ* must also be 1,nDCDs (within the ability of the GC analysis to differentiate the isomers). Only traces of m,nDCDs ($m \neq 1$) are produced. However, the **relative yields** of the 1,nDCDs produced by the two methods differ substantially. In addition to the pronounced difference in the major products from *in situ* dichlorination of nD (1,1DCD and 1,2DCD, eq 3) relative to the monochlorination of 1CD (1,12DCD), the ratio of yields of 1,1DCD to 1,2DCD produced by the two methods also differs substantially. For example, the ratio of 1,1DCD/1,2DCD (major products) produced from *in situ* dichlorination of nD adsorbed on NaLZ-105 is ca. 1, whereas the ratio of 1,1DCD/1,2DCD produced from the monochlorination of 1CD adsorbed on NaLZ-105 is ca. 3. This qualitative trend was found to hold for a range of conditions (Table 1).

These results are again readily accommodated by the working model if we accept the major sitings of nD, its *in situ* monochlorinated products, and 1CD to be the extended isomers in the linear channels, i.e., LIL and ILI. In the case of nD, there could be some 1CD, some 2CD, and traces of 3CD formed in the ILI site. The second chlorination could then occur *in situ*: at the 1- or 2-position of 1CD and at the 1-position of 2CD. On the basis of steric arguments, the ratio of 1,1DCD to 1,2CDC will be lower in this case than when one starts with only 1CD, since attack on the 2CD to yield 1,2DCD involves a more sterically accessible CH₃ group.

Sitings of the Compensating Cations. Having produced a working model that appears to be capable of rationalizing complex product distributions formed in the photochlorinations of nD and 1CD over a range of conditions, we now seek to extend the model to consider the sites of the compensating cations, since the product distributions are clearly a function of the nature of the compensating cation (Figures 3 and 4).

Although computational studies²¹ lead to conclusions concerning the most likely framework sites occupied by the negatively charged aluminum atoms, there have been few experimental or computational results that have been used to establish definitely the sites occupied by the cations, although it is expected that the siting of the cations will be relatively close to the Al sites in the framework. X-ray powder diffraction has been employed in an effort to establish the position of the ions.²² With Ni²⁺ cations it was found that the cation occupied two sites: one in a small cage above the sinusoidal channel

and the other in the sinusoidal channel near the intersection. However, these results are not directly pertinent to our work, since the bivalent ion must span between two aluminum centers.²³ In a study employing monovalent TI⁺ ions,²⁴ it was concluded that this cation occupied three sites, all in the intersections. One site is in the center of the intersection, while the other two are near the entrance to the linear channel. However, these zeolites were made by employing TPA ions and *n*-propanol as templates, and the investigation was performed by employing hydrated zeolites. Therefore, it is not clear that they are relevant to our investigation of the LZ-105 system.

Since nonpolar alkane molecules are expected to occupy, preferentially, channels which are cation-free to the extent possible, it is conceivable that the **chlorination studies reported here might allow the assignment of the positions occupied by the cations.** Using our model, it appears that the ions in LZ-105 might occupy sites very different from those found in zeolites made with organic templates. We conclude that the LIL and LIZ sites are occupied by nD, and the reason for this might be that it would be very difficult for nD to occupy the LIL and LIZ sites if the intersections were occupied and blocked by cations.

Now let us consider the detailed explanation of the cation effect on the selectivity parameters, based on the working model. For a fixed loading, as the size of the cation is increased, S_i increases to a maximum at potassium and then drops again as cation size continues to increase (Figure 3). The values of S_i are high for all of the alkali cations relative to silicalite and H-LZ-105 and are consistent with the hypothesis that when the linear channels and intersections are free of interfering cations, the sitings are relatively random. We expect the redistribution of the supramolecular isomers into the I and L sites from Z sites to be enhanced by increasing cation size, so the increase in S_i in the series silicalite, LILZ-105, NaLZ-105, KLZ-105 is readily explained by the model. Some other, currently unidentified, factor or factors must intervene with the largest cations, Rb and Cs. It may be that for the larger cations a reduced electrostatic interaction increases more rapidly than the steric interaction, so that the largest cations are not as capable of redistributing the supramolecular structures. However, from the results of the influence of cation size on S_i , it appears that this simple explanation may not be sufficient.

At a fixed loading S_i , the preference for 2- and 3-chlorination relative to 4-, 5-, and 6-chlorination increases monotonically with increasing cation size (Figure 4). This datum suggests a decrease in the ZIZ and ZIL populations, (which lead to production of 4-, 5-, and 6CDs) with increasing ion size. We conclude that the decrease in S_i for the largest ions, therefore, must be due to an increased population of the intersections (ILI, ILZ, and IZI). The decrease in ZIZ and ZIL sites would suggest that the percentage of LIZ sites drops relative to ILI sites. The increase in population of the intersection (I) sites would be unlikely if the intersections contained cations that had to be displaced. Thus, the results of both selectivity parameters as a function of cation size are generally consistent with the conclusion of an increased population of I- and L-containing sites occurring with increasing cation size, along with the decrease in Z-containing sites. **These conclusions are consistent with the hypothesis that the majority of the ions occupy the zigzag channels.**

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Although zigzag channels containing the ions are less hospitable to alkanes, it appears that alkanes can be forced to fit into them when the more favorable L and I sites are filled. As loadings are increased above 4%, S_t drops off. At these higher loadings there are too many alkane molecules for the more energetically favorable L and I sites, so that some alkanes are forced at higher loadings into the thermodynamically less desirable zigzag channels.⁸ We emphasize that there is no evidence to suggest that at the highest loadings employed in this paper substrate molecules are being chlorinated on the external surface of the zeolite. Therefore, **although siting in the zigzag channels is less favored than siting in the linear channels, the former is still favorable to siting on the external surface, which appears to be occupied only after essentially complete occupancy of the internal surface.**

The dichotomy between our conclusions about ion siting and those from X-ray analysis²⁴ for Ti^+ may be explained in at least two ways. The most likely explanation would be that templating zeolite growth with seed crystals leads to different siting of the framework aluminum atoms relative to organic templating. This could lead to different siting of the cations. A second possibility is that the ions themselves are mobile in the channels, leading to a change in siting when organic molecules are present. This is possible since there are three oxygens attached to the aluminum to which the ion could associate.

Conclusions

The photochlorination of nD adsorbed on the internal surface of a pentasil zeolite proceeds with a much higher selectivity for chlorination at the ends of the chain than for chlorination at the center. The selectivity is a function of variables such as the loading of the substrate (coverage of the internal surface), the nature of the compensating cation, and the number density of the compensating cations. These variations in selectivity are consistent with a model of the nD/Z complex consisting of an **outer layer** of supramolecular structures that is attacked more readily (than an **inner core layer**) by reagents ($\text{Cl}^\bullet/\text{Cl}_2$) which enter the crystal complex from the external surface and which attack mainly by diffusion through the **linear channels**. This mode of diffusion not only causes a preferred attack on the nD molecules in the outer layer but also causes a preferred attack on the structural isomers whose **proximal ends** are located in the linear channels or the intersections of the linear channels. This interpretation is consistent with the spirit of the proposal of molecular traffic control of the catalytic characteristics of size/shape selective zeolites such as pentasils.

This supramolecular model provides a simple and effective paradigm for the understanding of the following observations: (1) monochlorination of nD yields 1CD as the major product (attack of the reagents on the proximal ends of the nD molecules in the outer layer and in the linear channels); (2) dichlorination of nD yields 1,1DCD and 1,2DCD as the major products (attack

of the reagents on the proximal ends of 1CD and 2CD, which are selectively produced in the monochlorination step in the outer layer and in the linear channels); (3) monochlorination of 1CD yields 1,12DCD and 1,1DCD as the major products (attack of the reagents on the proximal methyl group of the 1CD molecule in the outer layer and on the distal chloromethyl group of the 1CD molecule in the outer layer); (4) dichlorination of nD begins long before complete conversion of the nD, and the rate of conversion falls off rapidly after a certain extent of monochlorination has occurred (attack of reagents is slowed down when the outer layer is monochlorinated). The latter observation is consistent with a model for which the monolayer of nD molecules, which are most readily attacked are in the outer layer, also protects the inner core layer from monochlorination. Thus, the monochlorinated species formed in the first layer undergo a dichlorination more rapid than monochlorination of the much larger number of nD molecules in the core layer.

The variation of selectivity as a function of loading and compensating cation can be explained in terms of redistribution of structures of the nD/Z complexes and in the occupancy of the outer layer and inner core as these variables are changed.

In terms of the supramolecular structural theory presented, the maximum in the selectivity as a function of loading and the influence of the cation on selectivity are explained as the result of redistribution of isomeric supramolecular structures which result from these variations. For example, the highest selectivity toward terminal chlorination of nD results from experimental conditions which promote the highest fraction of isomers of the LIL structure. The highest selectivity for formation of 1,12DCD results from conditions that favor the highest fraction of LILCl isomers.

Although the proposed model is consistent with the results, the supramolecular systems represented by the adsorption of a hydrocarbon in a zeolite possess considerable complexity so that further support for the validity of the working model is being sought through the use of other techniques, such as investigations of the supramolecular structure and dynamics of nD/Z isomers by multinuclear solid state NMR.²⁵ The structural ideas presented here allow zeolites to be considered as models for "solid enzyme systems" for which supramolecular interactions and controlled diffusion play a major role in the adsorption and catalytic characteristics.²⁶

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