

Molecular graphics and structural fitting of aromatics in large-pore zeolites

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We describe the usefulness of molecular graphics and structural fitting techniques as powerful and reliable tools for quick screening of zeolite catalysts for shape selectivity. The syntheses of 4,4'-diisopropylbiphenyl and p-isobutylethylbenzene are considered as case studies. Molecular graphics analysis of the isomers of diisopropylbiphenyl and isobutylethylbenzene in various zeolites indicates that large-pore zeolites are needed for the synthesis of these alkylaromatics. The importance of size and shape of the channels of large-pore zeolites is clearly brought out by the structural fitting technique. From the analysis of the results of molecular graphics studies and the structural fitting studies, it is inferred that ZSM-12 and mordenite are suitable zeolites for shape-selective production of diisopropylbiphenyl, and that offretite and mordenite are suitable zeolites for shape-selective production of p-isobutylethylbenzene. © 1999 by Elsevier Science Inc.

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INTRODUCTION

The application of molecular graphics to the study of protein crystallography¹ and medicinal chemistry² has enjoyed spectacular growth. Molecular graphics has been introduced to the study of catalysis, in an effort to understand the science behind catalysis.^{3–5} Another reason for the increasing use of molecular graphics involves the need for and benefit of computational analysis of experimental data. The availability of crystal structure databases⁶ combined with molecular graphics facilities to display them has opened the way for the rapid screening of a range of materials for potential catalytic applications. Occasionally, simple arguments based on molecular size and shape

may allow the investigator to derive an important insight into the steric interactions that underlie a catalytic process.

Zeolite research is one of the most rapidly developing fields in catalytic chemistry.⁷ These materials, based on silicon, aluminum, and oxygen as framework atoms, have complicated structures characterized by interconnected cavities and channels, presenting the ideal environment for shape-selective catalysis. The catalytic behavior of most of the zeolites arises from the catalytically active Brønsted acid sites. These active sites are located inside the intriguing pore structures. In such cases, molecular graphics can provide better understanding of the active sites. Molecular graphics can be used to provide an indication of the types of molecule that can be accommodated within the zeolite pores.

We have carried out a preliminary screening process, using molecular graphics, to identify the most suitable zeolite for the selective synthesis of 4,4'-diisopropylbiphenyl (DIBP). 4,4'-DIBP has a valuable application as an ingredient in liquid crystals and high-performance polymers.^{8,9} Separation of the isomers of DIBP is a difficult and costly process. So, there is a strong incentive for the development of a catalyst that would selectively produce 4,4'-DIBP. The shape selectivity in the alkylation of biphenyl with propene over few acidic zeolites with acidic sites such as faujasite (FAU), zeolite-L (LTL), mordenite (MOR), and ZSM-12 (MTW) has been reported.^{10,11}

HX and HY zeolites with the FAU framework structure have been used as disproportionating catalysts to convert *o*- and/or *m*-isobutylethylbenzene into *p*-isobutylethylbenzene (IBEB), which is an intermediate in the synthesis of α -(4-isobutylphenyl) propionic acid.¹² This substance is an anti-inflammatory drug, commercially known as ibuprofen. *p*-IBEB can also be synthesized by alkylation of isobutylbenzene with ethene over Lewis acid catalysts,¹³ in which the selectivity toward *p*-IBEB is typically 17.6%. The possibility of using zeolite catalysts for the production of *p*-IBEB by disproportionation of isobutylbenzene and a polyalkylbenzene over HY zeolite¹⁴ has been shown to lead to better selectivity (46.3%). Although HY zeolite is better than a conventional catalyst, selection of this specific zeolite is a random choice rather than

Color Plates for this article are on pages 169–176.

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a logical selection and no experimental results are available for any other zeolites.

Zeolites with a wide range of pore sizes are available. So, a screening process is desirable before actual catalytic testing in a reactor. More detailed applications of molecular graphics in the study of zeolite systems can be found in an article by Freeman *et al.*¹⁵ In the context of this background, we have analyzed the efficacy of various zeolites in the synthesis of 4,4'-DIBP and *p*-IBEB, using the molecular graphics method. It is possible to visualize rapidly how well the various reactant or product molecules fit inside the pores of zeolites.

METHODOLOGY

Before performing molecular graphics screening, a conformational search was carried out to find the minimum energy configuration of each of the molecules, and their flexibility. Using this method, various conformers of the molecule were generated by systematically varying the dihedral angle between the phenyl ring and the alkyl groups from 0 to 360 degrees in steps of 20 degrees. Energy minimization was performed for each conformer, using the consistent valence force field (CVFF) expression.¹⁶ The actual values of force field parameters used in the calculation are given elsewhere.¹⁷ The molecular graphics analysis and the force field energy minimization calculations are carried out with the INSIGHT II¹⁸ and DISCOVER¹⁹ software packages. All of the calculations were carried out on a Silicon Graphics Indigo 2 workstation. A space-filling²⁰ (CPK) model of each of the aromatics was placed inside the pores of zeolites and the position of each molecule was adjusted on the screen until the best fit between the molecule and zeolite was observed. We used the following radii for various atoms in the CPK representation: H = 1.10 Å, C = 1.55 Å, Si = 0.45 Å and O = 1.35 Å. The distance between the closest approaching atoms of the molecule and the zeolite was monitored to decide the best fit.

We performed molecular graphics screening of several large-pore zeolites, namely FAU, LTL, mazzite (MAZ), MOR, offretite (OFF), MTW, and cancrinite (CAN). The zeolite structures were taken from the crystal structure reported for FAU,²¹ LTL,²² MAZ,²³ MOR,²⁴ OFF,²⁵ MTW,²⁶ and CAN.²⁷ While fitting the molecules inside zeolites, the atoms in the zeolite lattice are assumed to be fixed at their crystallographically determined geometries.

RESULTS AND DISCUSSION

Molecular graphics analysis of molecules

All of the aromatic molecules are energy minimized by varying their geometry after building on the computer screen, in order to arrive at their minimum energy configurations. We performed molecular graphics screening with the minimized structures of the molecules. The size and shape of the molecules are critical parameters that decide the selectivity of the reaction. The molecular size of a guest molecule is usually characterized by a critical diameter, d_c ,²⁸ a Lennard-Jones length constant, s_m ,²⁹ or a minimum kinetic diameter of the molecule, d_m .³⁰ The critical molecular diameter is defined as the diameter of the cylinder that can circumscribe the molecule in its most favorable equilibrium conformation. The value of the Lennard-Jones length constant can be determined either from the transport

properties (viscosity, thermal conductivity) or from detailed measurements of the deviations from the ideal gas law (second virial coefficients).³¹ This method assumes a spherical shape for all of the molecules. When a molecule is within a cage of a zeolite, this Lennard-Jones length constant may give some indication of the interaction between the molecule and surrounding oxygen ions. The minimum kinetic diameter can be calculated from the minimum equilibrium cross-sectional diameter and is often used to characterize how difficult it is for a molecule to penetrate through a zeolite channel.³⁰

When the molecular diameter is close to, but still smaller than, the zeolite channel diameter, the molecule might experience a net attraction when passing through the channels. If the molecular diameter is slightly larger than the zeolite channel diameter, the molecule might experience a net repulsive force instead. If the molecular diameter is much larger than the channel diameter, the molecule can no longer enter the zeolite, owing to the strong repulsive force from the channels. Thus, it is an oversimplification to characterize a nonspherical molecule by critical diameter, Lennard-Jones length constant, or minimum kinetic diameter. Furthermore, the molecular sizes defined by the preceding methods pose problems; either they are too difficult to estimate or the estimated values are not reliable. For example, the critical diameters of 6.8 Å for *p*-xylene and 7.4 Å for *o*- and *m*-xylene³⁰ do not explain how zeolite ZSM-5 with a pore diameter of 5.1 to 5.4 Å is an efficient molecular sieve for their separation. Similarly, 1,3,5-triethylbenzene, with a critical diameter of 9.2 Å, diffuses in zeolites with 12-member (12-m) rings with diameters of 7.4 Å.³⁰ Thus, critical diameter has few drawbacks for consideration in molecular fitting. Hence, we adopt a method to describe the size and shape of the molecules as described elsewhere.³² The largest possible dimension of the molecules in three dimensions was considered. However, for the model to be close to reality, the molecules should neither be viewed as rigid spheres, nor should zeolite channels be viewed as rigid walls. This point is further discussed in the next section. In another interesting molecular dynamics study of the molecules inside zeolites, Yashonath and Santikary³³ have shown that there is a novel relation between the size of the molecule and the pore diameter. The diffusivity of the molecules inside zeolites is highest when they fit optimally within the pore of the zeolite.

Color Plate 1 shows biphenyl (BP) and the isomers of DIBP at their minimum energy configuration. Although the structure of biphenyl in gas phase is known to be nonplanar,³⁴ our calculations predict it to be planar. In fact, the rotational energy barrier between the planar and nonplanar configuration is negligible according to our calculations. In reality, there should be a small finite value. However, in the substituted biphenyl, we notice this difference and it is shown in Color Plate 1. The nonplanar configurations are more favorable than the planar configurations. The minimum energy configuration of ethylbenzene (EB), isobutylbenzene (IBB), and the isomers of IBEB are shown in Color Plate 2. For the energetically favorable conformation, the three largest dimensions ($a \times b \times c$) of the molecules are given in Table 1. Graphical representations of the atoms as spheres with their actual van der Waals radii provide the realistic size and shape of the molecule. Such a display of the zeolite framework atoms and sorbate molecules leads to the study of shape selectivity in zeolite-guest systems.

When correlating the dimensions of the molecules (Table 1) with the pore diameter of zeolites for molecular fitting pur-

Table 1. Dimensions of different organic molecules as derived from force field calculations

Molecule	Dimensions (Å)		
	<i>a</i>	<i>b</i>	<i>c</i>
4,4'-DIBP	13.85	6.77	4.36
4,3'-DIBP	12.44	5.87	5.05
3,3'-DIBP	10.61	6.54	5.50
EB	6.32	4.97	2.74
IBB	7.93	5.07	3.88
<i>m</i> -IBEB	8.45	5.95	5.55
<i>o</i> -IBEB	7.50	6.85	5.55
<i>p</i> -IBEB	10.47	5.22	4.46

poses, it is customary to neglect the largest dimension (*a*) of the molecules.³² The molecules prefer to enter the cages through their smallest dimensions on the basis of interaction energy criteria. Hence, only the other two dimensions (*b* and *c*) of the molecules need to be compared with the size of the pore openings. By comparing dimensions *b* and *c* of the molecules in Table 1, it is observed that "small-pore" zeolites (with 8-m rings) and "medium-pore" zeolites (with 10-m rings) with pore diameters of ~ 4.25 and ~ 5.25 Å, respectively, are too small to accommodate isomers of DIBP and IBEB, whereas "large-pore" zeolites (with 12-m rings) with pore diameters of ~ 7.25 Å are suitable for the diffusion of these molecules.

Molecular graphics analysis of zeolite catalysts

Zeolite channel diameter cannot be described by a precise number. In the case of zeolites, various radii of oxygen, such as 1.30 Å (Flanigen *et al.*²⁹) 1.35 Å (Olson *et al.*³⁵), and 1.40 Å (Ruthven³⁶), were used, which could result in different diameters for the same pore. The calculation of the free diameter of a zeolite channel also depends slightly on the choice of diametrically opposing oxygens.²⁹ The vibration of the crystal lattice and the possible distortions of both molecule and zeolite when the molecule penetrates through the lattice make it even more difficult to assess the precise diameter of either molecule or zeolite pore. Several excellent molecular dynamic studies^{37–39} shed more light on this complicated phenomenon, including pore aperture dimension variations in real time.

Color Plate 3 shows the cross-section of the pores in FAU, LTL, MOR, MTW, MAZ, OFF, and CAN, which are relevant to molecular shape-selective catalysis. The zeolite FAU has framework structure²¹ consisting of linked β or sodalite cages. A sodalite cage structure is made up of 24 tetrahedra arranged as six four-ring faces and eight six-ring faces in a cagelike fashion. Linking sodalite cages by double six-rings through four of the eight six-ring faces in tetrahedral arrays results in the framework structure of FAU. FAU, apart from having β cages, also has hexagonal prisms formed by double six-rings and supercages with a twelve-member ring entrance window. LTL also has a twelve-member channel which extends along the *c* axis.²² Its framework is made up of polyhedron cages called *cancrinite* cages. In the LTL topology, cancrinite cages are joined to three neighboring cages via oxygen bridges to

form 8-m ring and circular 12-m ring channels in the stacking direction. The diameter of the larger channel increases between the 12-m ring windows, giving the channel an undulating character. Although 8-m rings are present in orientations both parallel and perpendicular to the 12-m ring channels, they are so much distorted that for all practical purposes only a one-dimensional 12-m ring channel system is available for molecular motion. In MOR topology²⁴ units of four 5-m rings are joined to one another via common edges to form chains. Mirror images of these chains are connected to form corrugated sheets. Finally, sheets displaced by half a translation are connected to one another via oxygen bridges to form elliptical 12-m ring channels and 8-m rings along the corrugations. The 8-m ring openings of adjacent 12-m ring channels are displaced with respect to one another, so that the 8-m ring channel is tortuous. Consequently, the channel system is essentially one dimensional. The MTW structure²⁶ contains a 12-m ring as the largest opening, which is highly nonplanar. In the MAZ structure²³ two types of smaller channels are present in addition to the main 12-m ring channel: the first consists of stacked gmelinite cages leading to 6-m rings; the second is between two cross-linked rows of cages leading to 8-m rings. In the OFF structure²⁵ 4-m rings, 6-m rings, and 8-m rings are present and surround the main 12-m ring channel. The 8-m rings in the *b* direction have free diameters of 5.2×3.8 Å and form narrow gates to the 12-m ring channel in the *c* direction. The main feature of CAN²⁷ resembles OFF, except that the diameter of the 12-m ring channel is smaller. The crystal characteristics of the zeolites previously mentioned and their pore diameters are summarized in Table 2.

Structural fitting

Color Plate 4 shows CPK views of 4,4'-, 4,3'-, and 3,3'-DIBP in LTL. The pore of LTL appears to have plenty of empty space for each of the molecules. Hence LTL would not be expected to produce 4,4'-DIBP selectively. Color Plate 5 shows CPK views of the isomers of DIBP in MOR. In contrast to the LTL pore, there is much less empty space for each of the molecules in the MOR pore. Moreover, 4,4'-DIBP fits slightly better in the cross-section of the MOR channel. This indicates that MOR would be a better shape-selective catalyst than zeolite L. The CPK views of the three isomers of DIBP in MTW are shown in Color Plate 6. 4,4'-DIBP has a compact cross-section by virtue of the fact that the three bulky components (the two isopropyl groups and the biphenyl ring) are

Table 2. Crystal characteristics of various large-pore zeolites

Zeolite	Symmetry	Unit cell composition	Pore diameter (Å)
FAU	Cubic	[SiO ₂] ₁₉₂	7.4
LTL	Hexagonal	[SiO ₂] ₃₆	7.1
MOR	Orthorhombic	[SiO ₂] ₄₈	6.5 × 7.0
MTW	Monoclinic	[SiO ₂] ₂₈	5.7 × 6.2
MAZ	Hexagonal	[SiO ₂] ₃₆	7.4
OFF	Hexagonal	[SiO ₂] ₁₈	6.7
CAN	Hexagonal	[SiO ₂] ₁₂	5.9

arranged linearly. In contrast, these components are not arranged linearly in the 4,3' and 3,3' isomers. With one isopropyl group placed on the side of the biphenyl ring in the 4,3' isomer and both isopropyl groups on the same side of the biphenyl ring in the 3,3' isomer, these two isomers are less well packed in the channel of MTW. For all three isomers there is some overlap of the atoms of DIBP molecules with the zeolite framework. However, in the case of the 4,4' isomer there is a significant amount of space between the molecule and the atoms of the zeolite framework in certain orientations. The diffusion of 4,3' and 3,3' isomers will be significantly impeded by steric interactions with the atoms forming the MTW channel. Thus MTW is expected to show better selectivity for 4,4'-DIBP.

The molecular graphics method can be extended to study the fitting of alkylbenzenes such as ethylbenzene, isobutylbenzene, and isomers of isobutylethylbenzene. Color Plates 7–13 show the molecular graphics fitting of the three isomers of IBEB in various large-pore zeolites. It is apparent from Color Plates 7–13 that all three isomers can easily diffuse through the pores of FAU (Color Plate 7), LTL (Color Plate 8), and MAZ (Color Plate 9). In these cases, the fit for *o*- and *m*-IBEB does not appear to be noticeably worse than that for the *p*-isomer, although *o*-IBEB can have only restricted orientations. In the case of MOR (Color Plate 10), *p*-IBEB fits more freely than *m*-IBEB, whereas *o*-IBEB fits tightly. The pore sizes of OFF (Color Plate 11), MTW (Color Plate 12), and CAN (Color Plate 13) are slightly smaller. In the case of OFF (Color Plate 11), *p*-IBEB fits freely, whereas *m*- and *o*-IBEB fit tightly. Thus MOR and OFF are expected to show better selectivity for *p*-IBEB. In the case of MTW (Color Plate 12) and CAN (Color Plate 13), all of the isomers of IBEB fit tightly. This suggests that there could be significant difficulty for diffusion of the three isomers in these zeolites. A visual inspection of the fit of the IBEB isomers inside the pores of various zeolites in Color Plates 7–13 indicates that zeolites with large elliptical pores (ca. MOR) are the best candidates for selective production of *p*-IBEB.

CONCLUSIONS

Molecular graphics can be used to increase our understanding of zeolite structure and to develop an interaction model between zeolite structure and sorbate molecules. It provides a preliminary screening of possible zeolite catalysts for a specific reaction before further detailed calculations or experiments are performed.

In this work, we have used molecular graphics to understand the intriguing pore architecture of several large-pore zeolites. This method has been applied to study the structural fitting of the aromatic molecules inside these zeolites to understand their shape-selective properties. Further, molecular graphics can be used to analyze the different configurations and orientations of molecules inside the zeolites during the course of diffusion. From the analysis of the results of molecular graphics studies and structural fitting studies, it is inferred that MTW and MOR are suitable for shape-selective production of 4,4'-DIBP. This result coincides with an earlier report,¹¹ in which MTW was found to be the most suitable shape-selective zeolite. Our studies indicate that MOR and OFF are better shape-selective catalysts for the production of *p*-IBEB than is FAU, whereas reports on experimental studies are available only for FAU.¹³

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