Theoretical analysis of the coverage dependence of enantioselective chemisorption on a chirally templated surface

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The effect of the formation of ensembles of chiral templates on the enantioselectivity of model heterogeneous catalysts is studied theoretically in the framework of a cooperative sequential adsorption model. Analytical solutions are presented for random adsorption onto a chirally templated surface which indicate that the surface exhibits a maximum enantioselectivity of $\sim$2.5, in agreement with results of enantioselective chemisorption experiments carried out in ultrahigh vacuum. It is suggested that the high enantioselectivity ($\gtrsim$90%) encountered in commercial catalysts could be due to correlated adsorption of the template molecules, and that these effects can be modeled using Monte Carlo calculations. © *2003 American Institute of Physics.*
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I. INTRODUCTION

In view of the increasing demand for heterogeneous, enantioselective catalysts for drug synthesis, there has been a renewed interest in understanding the structures of catalyst modifiers that lead to enantioselectivity.[1,2] This has been spurred by the paucity of enantioselective catalytic systems that have been developed empirically so that a fundamental understanding of the requirements for chiral templating species becomes all the more important. A common thread running through all of the results on enantioselective catalytic systems is the observation that significant enantioselective excesses ($\gtrsim$90%) are only achieved over a relatively narrow coverage range;[3–5] slightly larger or smaller coverages of the templating species lead to a significant decrease in the enantioselectivity of the reaction. A similar effect has been found for the enantioselective chemisorption of propylene oxide on a Pd(111) surface that has been chirally templated with 2-butanol, which reacts to form 2-butoxide species on the surface.[6] In this case, enantioselective chemisorption of *R*- or *S*-propylene oxide on a 2-butoxide-templated Pd(111) surface also only appeared over a narrow coverage range, and higher or lower 2-butoxide coverages lead to nonenantioselective chemisorption. Thus, the model system probed in ultrahigh vacuum mimics the coverage dependence of the working catalytic systems. The correlation between the catalytic and chemisorption experiments can be understood if enantioselectivity is induced by affecting the way in which the reactant adsorbs onto the surface, rather than later in the reaction. While this need not necessarily be the predominant cause in heterogeneous enantioselective catalysis, a theoretical study of the implications of this assumption is presented in the following using a variation of the widely studied cooperative sequential adsorption (CSA) method.[7,8]

It is proposed that there are at least two basic requirements for a chiral template molecule to exert an effect on the adsorption of a probe molecule that enables it to exhibit enantioselectivity. The first is the existence of a particular adsorption geometry that the chiral template species adopts on the surface. Second, since the probe molecule adsorbs onto the metal surface between the chiral templating overlayer, so that the probe molecule adsorbs into chiral pockets defined by an overlayer of the templating molecule,[2,9] variations in the number of these pockets as a function of coverage of the template molecule will control the variation in enantioselectivity as a function of coverage of the template molecules.

In the enantioselective adsorption experiments,[6] 2-butanol was chosen as a simple chiral template molecule, which is anchored to the surface by dissociation of the O–H bond to form an alkoxide. The carbon atom attached to this group provides the chiral center. However, if the chiral template molecule can rotate relatively freely about the bond attaching the chiral center to the surface (in the case of the butoxide species, the bond between the oxygen and the chiral carbon), it is unlikely that the chirality will be expressed. Thus, for a freely rotating system, any asymmetry in the chiral center will be completely averaged out by free rotation about this axis. However, even if the chiral template is not completely free to rotate but is sufficiently mobile such that the probe chemisorbing molecule can cause it to move or reorient, any steric effect that the template will be able to exert on the probe molecule will be lost, resulting in an overlayer that does not lead to enantioselective chemisorption.

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These effects will depend on the temperature at which experiments are carried out and the relative heat of adsorption of the probe molecule compared to the energy required to rotate the functional groups of the chiral patterning molecule about its chiral center. In the case of experiments on the enantioselective adsorption of propylene oxide on 2-butanol-patterned Pd(111), the structural rigidity of the template species need not be high since experiments were carried out at 80 K, thus minimizing thermal motion, and propylene oxide adsorbs only relatively weakly. Recent density functional calculations carried out in our laboratory suggest that the carbon chain of the butoxide species is stabilized by interaction with the surface so that it is oriented essentially parallel to the Pd(111) plane. Clearly, however, in the case of chemisorption carried out at higher temperatures, or with more strongly bound probe molecules, the chiral center should be more strongly attached to the surface to prevent it moving. A similar point has been made in investigations of tartaric acid as a chiral template, where it was suggested that interactions of both acid groups in the tartaric acid with the surface were required to provide an effective chiral template overlayer.[2,9] This suggests that chiral templating molecules not only require a means of anchoring them to the surface, as suggested above, but also a second point of coordination to the surface to allow the chirality to be expressed.

The experimentally observed variation in enantioselectivity with template coverage could be due to two effects. The first could arise from a change in adsorbate geometry with coverage, resulting in a change in molecular conformation as discussed above.[2] Certainly, there are many examples in the literature of adsorbates that change geometry as a function of coverage. It has also been suggested that a change in conformation is, at least partially, responsible for the gain or loss of enantioselectivity in cinchonidine-modified hydrogenation catalysts.[5,10,11] The second effect, particularly in cases in which the chiral pocket is defined by an ensemble of chiral templates, could be due to the variation in the number of these chiral pockets as a function of the chiral template coverage. This effect is the subject of the following paper. It is intuitively clear that this will have a profound effect on the coverage variation of the chiral template molecule's enantioselectivity since, at low coverages, relatively few chirally active ensembles (pockets) will have formed, resulting in nonenantioselective adsorption, and that the relative concentrations of different chiral ensembles will vary in different ways with coverage. While the structure of the chiral-template overlayer will depend in detail on the nature of the lateral interactions between the molecules, in the following it is initially assumed for simplicity that the chiral patterning molecules adsorb randomly into fixed sites on the surface. Subsequent analyses take account of the interaction between molecules already adsorbed on the surface on the variation of enantioselectivity with coverage using Monte Carlo methods.

II. DESCRIPTION OF THE MODEL

The model uses a two-dimensional array of adsorption sites with a fourfold connectivity employing periodic boundary conditions as shown in Fig. 1. We have previously dem-
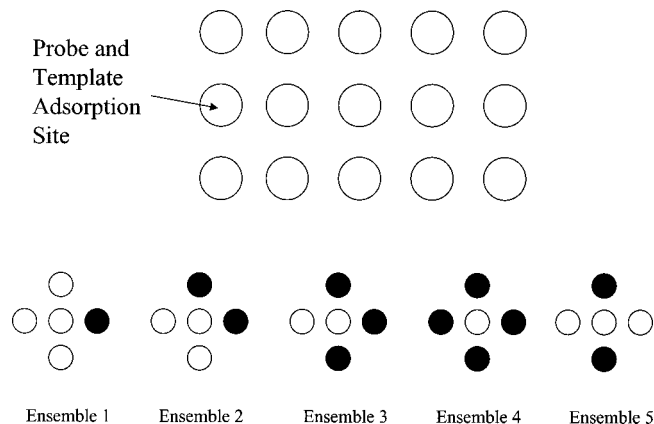

FIG. 1. Schematic diagram showing the arrangement of chiral templates molecules and the chiral probe adsorption sites on a rectangular surface. Shown also are the possible ensembles of template adsorption sites around the chiral probe site.

onstrated that a chiral overlayer (consisting of 2-butanol) affects the adsorption of chiral probes composed of propylene oxide.[6] The enantioselective chemisorption varies with template coverage and reaches a maximum, decreasing once again at higher template coverages. This implies that the template molecules form chiral pockets which preferentially allow docking of one enantiomer of the probe molecule. However, little is currently known about the details of the structures of these overlayers. Thus, in order to illustrate strategies for analyzing these effects, a simple model is taken in which both chiral template and probe molecules can adsorb at the same sites on the surface. Finally, two adsorbates are not allowed to occupy a single site, so that adsorption only into the first layer is considered. Such a fourfold array is chosen to simplify statistical calculations and could mimic adsorption on a square ensemble [e.g., on a (100) surface], a rectangular ensemble [e.g., on a (110) surface], or a diamond-shaped ensemble [e.g., on a (111) surface]. The process consists of two stages: first, a given coverage of the template molecules is established. As the surface becomes covered by chiral template molecules, several environments will appear around the chiral adsorption site. These are also shown in the bottom drawing of Fig. 1 and labeled ensemble 1 through 5. An ensemble with no template molecule is not shown but is included in the calculation. The total coverage of the chiral template molecules is given by Θ_T. The enantioselectivity is then calculated in two ways:

(i)   A constant flux of a racemic mixture of chiral probe molecules is incident onto the surface where, on hitting a chiral pocket, molecules of R chirality adsorb with probability q and molecules with S chirality adsorb with probability $1-q$.[12]

(ii) The surface covered by the template is first exposed to a flux of one enantiomer of the probe molecules, then emptied of probe molecules, and subsequently exposed to the other enantiomer.

In order to probe the effect of each ensemble, only one ensemble shown in Fig. 1, labeled i ($i=1$ to 5), is taken to

be enantioselective (with adsorption probability q), while the remainder of the sites are taken to be completely nonenantioselective. If several ensembles are enantioselective, the net effect is calculated merely by summing the effect of each ensemble. The enantioselectivity S_i of the surface due to the ith ensemble is calculated from the ratio of the coverage of the R enantiomer of the probe molecule (Θ_P^R) to the coverage of the S enantiomer (Θ_P^S) as a function of template coverage (Θ_T), so that

$$S_i = \frac{\Theta_P^R}{\Theta_P^S}. \tag{1}$$

III. ANALYTICAL THEORY: RANDOM ADSORPTION

A. Exposure to a racemic mixture of chiral probe molecules

In the case in which the template molecules adsorb completely randomly onto the surface, the probability of formation of each of the ensembles shown in Fig. 1, P_i ($i = 1$ to 5), can be calculated analytically as

$$P_1 = 4\Theta_T(1-\Theta_T)^3, \tag{2}$$

$$P_2 = 4\Theta_T^2(1-\Theta_T)^2, \tag{3}$$

$$P_3 = 4\Theta_T^3(1-\Theta_T), \tag{4}$$

$$P_4 = \Theta_T^4, \tag{5}$$

$$P_5 = 2\Theta_T^2(1-\Theta_T)^2, \tag{6}$$

and P_0 is the probability that a site has four empty neighbors, where

$$P_0 = (1-\Theta_T)^4. \tag{7}$$

If the surface is exposed to a racemic mixture of probes molecules, the total number of surface adsorbates n at some time is given by:

$$n = n_T + n_P^R + n_P^S, \tag{8}$$

where n_T is the total number of chiral template molecules (and does not change with time), n_P^R is the number of R-probe molecules, and n_P^S the number of S-probe molecules. After the surface has been completely covered by probe molecules, then

$$\Theta_T + \Theta_P^R + \Theta_P^S = 1, \tag{9}$$

where $\Theta_X = n_X/M$, where M is the total number of sites on the surface. Focusing on adsorption onto the ith ensemble, which is taken to be enantioselective while the rest are not, then the number of R-probe molecules on the surface is given by

$$n_P^R = n_P^R(i) + \sum_{j \neq i} n_P^R(j), \tag{10}$$

where the indices in parentheses refers to the ensemble. Equation (10) shows that the total number of R-probe molecules on the surface is the sum of all of those adsorbed on

the sites defined by the ensembles shown in Fig. 1, plus all the ensembles with empty sites. A differential change in coverage is given by

$$\delta n_P^R = \delta n_P^R(i) + \sum_{j \neq i} \delta n_P^R(j). \tag{11}$$

Let the number of racemic probe molecules delivered to the surface per unit time be F_P. For convenience, F_P is set equal to M, the number of probe adsorption sites on the sample, so that unit time is defined as that required to deliver M molecules to the surface. Thus, in a racemic mixture, the differential change in the number of R- and S-probe molecules delivered to the surface, δF_P^R and δF_P^S, respectively, in time δt is given by

$$\delta F_P^R = \delta F_P^S = \tfrac{1}{2} M \delta t, \tag{12}$$

where t is the time and M the total number of sites. Last, the number $N(j)$ of vacant sites surrounded by ensemble j, are considered

$$N(j) = (M - n_T)P_j, \tag{13}$$

where $(M - n_T)$ is the number of sites not occupied by template molecules.

Taking the number of probe molecules already adsorbed at the ith site to be $n_P(i)$, then the number of vacant sites of type "i" is $N(i)-n_P(i)$, so that the proportion of sites that are vacant is $(N(i)-n_P(i))/M$. Taking the probability of adsorption of an R-probe molecule onto this site to be q, then the additional number of molecules that adsorb onto these sites $\delta n_P^R(i)$ when an additional δF_P^R impinges onto the surface is given by

$$\delta n_P^R(i) = \left[\frac{(N(i) - n_P(i))}{M} q \right] \delta F_P^R, \tag{14}$$

where $n_P(i) = n_P^R(i) + n_P^S(i)$. Rewriting Eq. (14), taking into account Eq. (12), yields

$$\frac{d\Theta_P^R(i)}{dt} = \frac{1}{2}(\Theta(i) - \Theta_P(i))q, \tag{15}$$

where $\Theta(i) = N(i)/M$ and $\Theta_P(i) = n_P(i)/M = \Theta_P^R(i) + \Theta_P^S(i)$. An analogous equation can be written for the coverage of the S-probe species as

$$\frac{d\Theta_P^S(i)}{dt} = \frac{1}{2}(\Theta(i) - \Theta_P(i))(1-q). \tag{16}$$

Thus, from Eqs. (15) and (16), it is evident that

$$\frac{1}{1-q}\Theta_P^S(i) = \frac{1}{q}\Theta_P^R(i), \tag{17}$$

which allows the maximum coverages of the R and S probes to be related to the number of the different ensembles on the surface. Converting Eq. (13) into coverage, and using the fact that $n_P(i) = n_P^R(i) + n_P^R(i)$, then

$$\Theta(i) = (1-\Theta_T)P_i = \Theta_P^R(i) + \Theta_P^S(i). \tag{18}$$

Solving the simultaneous Eqs. (17) and (18) yields

$$\Theta_P^R(i) = q(1-\Theta_T)P_i, \tag{19.1}$$

and

$$\Theta_P^S(i) = (1-q)(1-\Theta_T)P_i. \tag{19.2}$$

A similar set of equations analogous to Eq. (13) can also be written for the number of R probes adsorbing on the remaining nonenantioselective sites as

$$\sum_{j \neq i} \delta n_P^R(i) = \sum_{j \neq i} \left[\frac{(N(j) - n_P(j))}{M} \right] \delta F_P^R, \tag{20}$$

which can be rewritten, using Eq. (12), as

$$\sum_{j \neq i} \frac{d\Theta_P^R(j)}{dt} = \frac{1}{2} \sum_{j \neq i} (\Theta(j) - \Theta_P(j)), \tag{21}$$

and similarly for the adsorption of the S-probe molecules

$$\sum_{j \neq i} \frac{d\Theta_P^S(j)}{dt} = \frac{1}{2} \sum_{j \neq i} (\Theta(j) - \Theta_P(j)). \tag{22}$$

Thus, from Eqs. (21) and (22), for nonenantioselective sites

$$\sum_{j \neq i} \Theta_P^R(j) = \sum_{j \neq i} \Theta_P^S(j). \tag{23}$$

Taking Eq. (23) into account shows that

$$\sum_{j \neq i} \Theta_P(j) = \sum_{j \neq i} (\Theta_P^R(j) + \Theta_P^S(j)) = (1-\Theta_T)(1-P_i), \tag{24}$$

so that

$$\sum_{j \neq i} \Theta_P^R(j) = \sum_{j \neq i} \Theta_P^S(j) = \tfrac{1}{2}(1-\Theta_T)(1-P_i). \tag{25}$$

Thus, the total coverage due to adsorption at both enantioselective and nonenantioselective sites is

$$\Theta_P^R(i) = \tfrac{1}{2}(1-\Theta_T)(1-P_i) + q(1-\Theta_T)P_i$$
$$= (1-\Theta_T)[\tfrac{1}{2} + P_i(q - \tfrac{1}{2})] \tag{26}$$

and

$$\Theta_P^S(i) = \tfrac{1}{2}(1-\Theta_T)(1-P_i) + (1-q)(1-\Theta_T)P_i$$
$$= (1-\Theta_T)[\tfrac{1}{2} - P_i(q - \tfrac{1}{2})]. \tag{27}$$

Thus, by substituting into Eq. (1) the enantioselectivity of the ith ensemble is simply given by

$$S_i = \frac{1 + P_i(2q-1)}{1 - P_i(2q-1)}. \tag{28}$$

This equation is shown plotted for each of the five ensembles versus template coverage Θ_T in Fig. 2 for $q = 1.0, 0.9, 0.8, 0.7,$ and 0.6. Clearly, for $q = 0.5$, there is no enantioselectivity since each of the enantiomers adsorbs with equal probability. This trend is further seen in the decreasing enantioselectivity for each site with decreasing q, as expected. Evidently the enantioselectivity varies as a function of template coverage where ensemble 1 shows the maximum enantioselectivity at $\Theta_T = 0.25$ ($S \sim 2.5$, $q = 1$), and ensemble 3, being the structural mirror image of ensemble 1, shows a similar maximum in the enantioselectivity at $\Theta_T = 0.75$. En-

sembles 2 and 5 have their maximum enantioselectivities at $\Theta_T = 0.5$, with ensemble 2 having a maximum enantioselectivity of ~ 1.6 and ensemble 5 having a value of ~ 1.3. These ensembles exhibit modest values of enantioselectivity since they are present in relatively low proportions as the surface fills with template molecules. Ensemble 4 is the only one that displays high enantioselectivities as the template coverage approaches saturation, since at $\Theta_T = 1.0$, the surface is exclusively covered by these ensembles. In fact, Eq. (28) predicts that $\lim_{\Theta_T \to 1} S = \infty$ for $q = 1$. This problem can be solved by introducing defect sites regions, where it can easily be shown that Eq. (28) converts into

$$S = \frac{1 + P_i(2q-1) + \alpha}{1 - P_i(2q-1) + \alpha}, \tag{29}$$

with $\alpha = \Theta_D / \Theta_C$, where Θ_D represents the coverage of template defect sites and Θ_C the coverage of enantioselective template sites so that $\Theta_T = \Theta_D + \Theta_C$. As an example, if $\alpha = 0.1$, then the enantioselectivity of ensemble 4 would be ~ 21 at saturation coverage.

B. Sequential adsorption of chiral probe molecules

In the case of *sequential* adsorption of the chiral probe molecules, where a template-covered surface with coverage Θ_T is first exposed to R-probe molecules, then emptied of probe molecules, and then exposed to S-probe molecules, then when $q = 1$

$$\Theta_P^S(i) = (1-\Theta_T)(1-P_i), \tag{30}$$

so that the enantioselectivity, in this case, is given by

$$S_i = \frac{1}{1 - P_i}. \tag{31}$$

A similar variation in enantioselectivity, compared with exposure to a racemic mixture of probe molecules, is found in this case (Fig. 3), where a maximum value of $S \sim 1.7$ is found except for the ordered ensemble 4, which tends to infinity as the template coverage approaches saturation.

These results suggest that a requirement for a highly enantioselective catalysts that is capable of yielding enantioselectivity values greater than ~ 2.5 is to form ordered structures with enantioselective pockets, but still be sufficiently open that it allows the chiral probe molecule to adsorb. Thus, the maximum enantioselectivity that can be expected for random adsorption of template molecules is ~ 2.5. This implies that an additional requirement for an effective chiral template, as suggested in the supramolecular assemblies of R,R-tartaric acid,[9] is that the interadsorbate interactions be such that they form uniform, ordered structures at intermediate coverages that are sufficiently open to allow the probe molecule to adsorb onto the surface in their presence. Modeling interacting templated surfaces requires more detailed Monte Carlo techniques, which will be illustrated in subsequent sections.
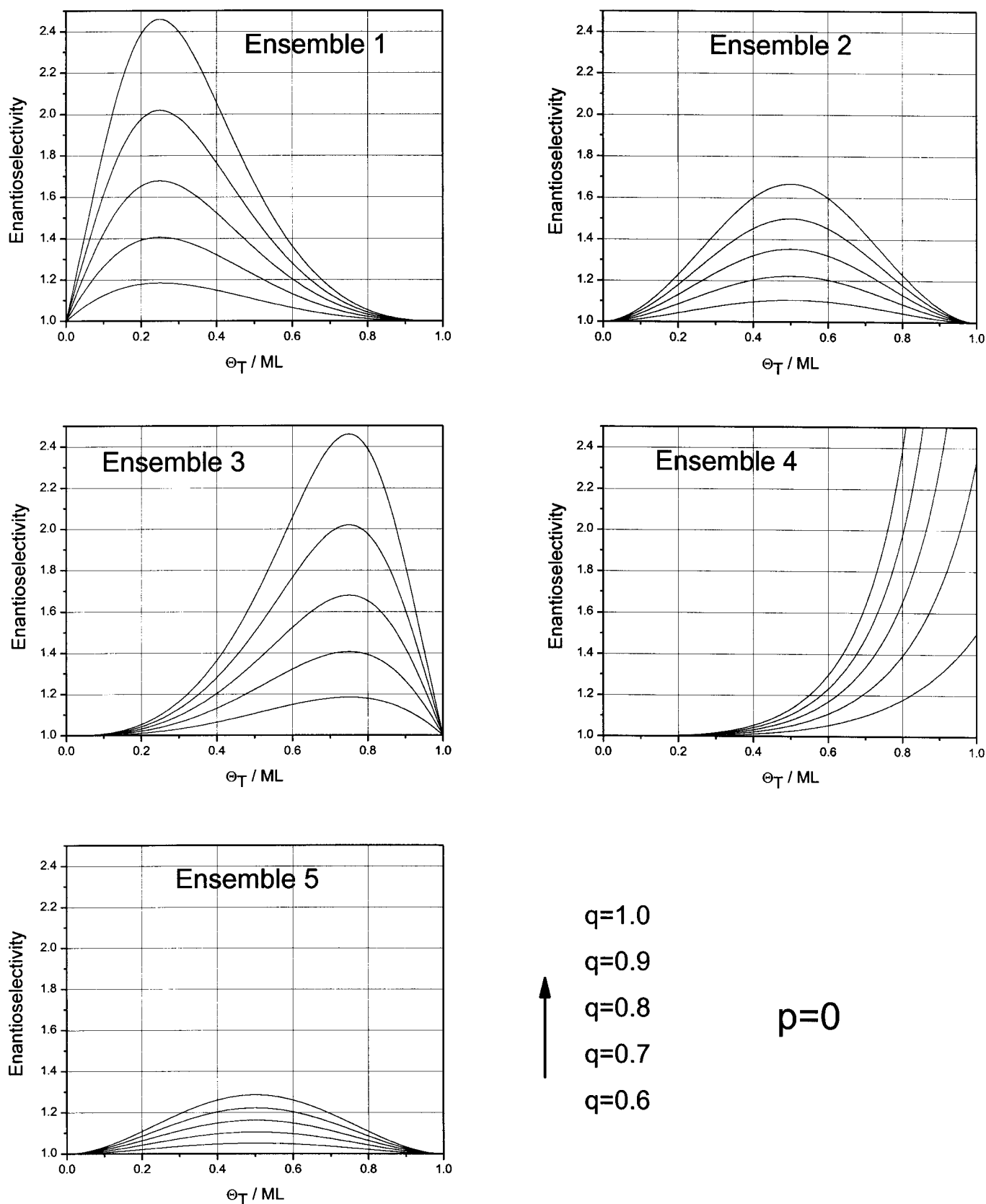
Analytical
(mixed probe adsorption)

FIG. 2. Plots of the analytical solutions for adsorption of a racemic probe mixture on an uncorrelated chiral template on the rectangular surface as a function of template coverage, Θ_T, for each of the ensembles shown in Fig. 1 as a function of q, the probe molecule adsorption probability.
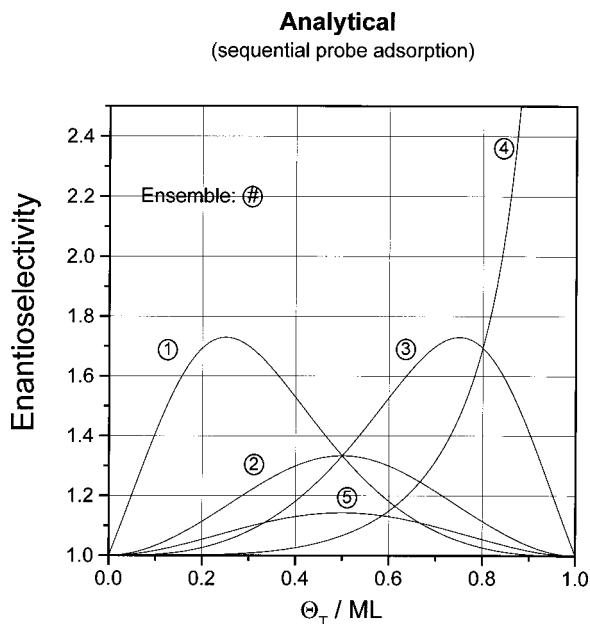
Analytical
(sequential probe adsorption)

FIG. 3. Plots of the analytical solutions for sequential adsorption of chiral probes on the rectangular surface as a function of template coverage, Θ_T, for each of the ensembles shown in Fig. 1.

FIG. 4. Plot of the coverage of the template molecules, Θ_T, as a function of Monte Carlo time for correlated adsorption for different values of p. The exact solution for random adsorption ($p=0$) is shown for comparison as a full line.

IV. MONTE CARLO THEORY: CORRELATED ADSORPTION

In this case, correlation between the adsorption of template molecules is introduced very simply by assuming that the probability P_T that a template molecule adsorbs onto a vacant site is given by

$$P_T = 1 - \nu p, \tag{32}$$

where ν is the number of nearest neighbors and p can take values between 0 and 0.25. The case of $p=0$ corresponds to random adsorption on the surface and can be solved analytically as shown in the previous section. The enantioselectivity in the case of correlated adsorption is followed, as above, by exposing the surface to a racemic mixture of probes molecules which adsorb with probability q if they have the same chirality as the template and $1-q$ if they are of the opposite chirality. The Monte Carlo[13] calculations were carried out using the two stages described above, on a two-dimensional lattice of connectivity four, with periodic boundary conditions. Figure 4 shows the adsorption kinetics of the template species onto the surface as a function of Monte Carlo time measured in Monte Carlo steps (MCS). One MCS is a number of adsorption trials equal to the number of adsorption sites. The data for $p=0$ ($\square$) are in excellent agreement with the analytical theory (full line), confirming that the Monte Carlo simulations have converged. The enantioselectivity is plotted for various values of p in Fig. 5 for $q=1$ (random adsorption). In the case of ensembles containing a small number of template molecules (e.g., ensembles 1, 2, and 5), correlated adsorption has a relatively minor effect on the variation in enantioselectivity with coverage. Effects due to correlation become more marked in the case of ensembles containing larger number of atoms (for example, ensemble
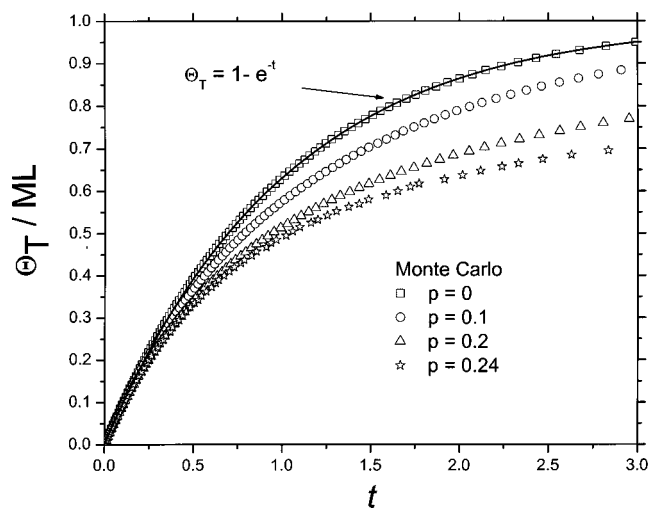
3), where this reaches a maximum at $\Theta_T = 0.75$ for random template adsorption ($p=0$, Fig. 2 and solid line, Fig. 5) but shifts to $\Theta_T = 0.6$ for $p=0.24$ (▲) (Fig. 5).

V. DISCUSSION

It is proposed that the efficacy of a chiral template molecule depends both on the local molecular geometry[5,10,11] as well as the arrangement that the molecules adopt on the surface.[2,7] In addition to possessing a chiral center and being bonded to the surface, it is suggested that the template molecule should be anchored by, at least, a second point in the molecule to prevent it from rotating relatively freely, causing the asymmetry due to the chiral center to be averaged out.[2,6] A simple model that assumes that a single ensemble of chiral template molecules on the surface can act to form enantioselective pockets for the adsorption of a chiral probe molecule shows that the enantioselectivity varies from unity over a relatively narrow coverage range (Figs. 2, 3, and 5). This is in general agreement with catalytic results in which the enantioselectivity maximizes over a narrow range of template coverages[3–5] and with chemisorption data in ultrahigh vacuum where the chemisorption of R- or S-propylene oxide on a surface covered by R-2-butoxide species varies significantly with coverage.[6] The simulation results reveal that the maximum enantioselectivity reaches ~ 2.5 for ensembles 1 and 3 for $q=1$ at coverages of 0.25 and 0.75, respectively. This is within the range found for enantioselective adsorption on a chirally templated surface in ultrahigh vacuum,[6] but much lower than found catalytically for the best systems. This is likely due to the fact that more uniform ordered structures are formed in these cases to produce a surface with a larger relative concentration of chiral pockets. These initial results, however, do demonstrate the efficacy of Monte Carlo strategies for effectively modeling enantioselective adsorption on surfaces.

Monte Carlo
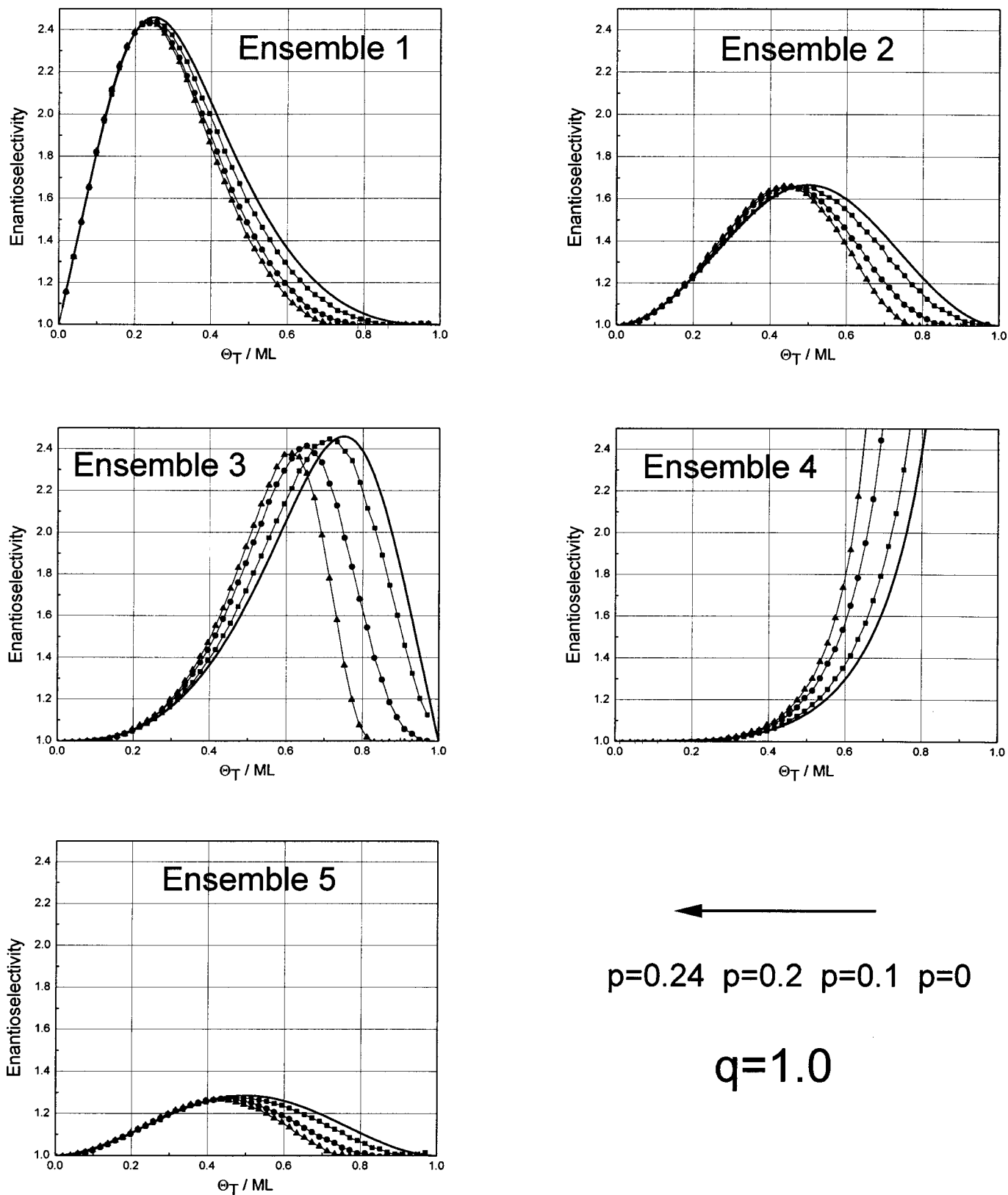## (mixed probe adsorption)

FIG. 5. Plots of the enantioselectivity, following exposure to a racemic mixture of the probe molecules, calculated using Monte Carlo methods, as a function of template coverage, Θ_T, for the ensembles depicted in Fig. 1, as a function of template correlation with $p=0$ (full line), 0.1 (■), 0.2 (●), and 0.24 (▲).

VI. CONCLUSIONS

It is proposed that the ability of a chiral template overlayer to affect the adsorption enantioselectivity of a probe molecule depends on the local adsorption geometry of the template molecule as well as the ordered structures that it forms on the surface. It is illustrated how the enantioselectivity of the template overlayer can be investigated theoretically as a function of overlayer coverage both analytically, in the case of random adsorption onto the surface, and by using Monte Carlo strategies in the case of correlated adsorption. Preliminary results showing the variation of template coverage required to maximize the enantioselectivity (Fig. 5) demonstrate how the enantioselectivity varies as a function of template adsorption correlation.

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