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TESTING SITE SIZE REQUIREMENTS IN CHEMISORPTION: EXPERIMENT AND THEORY

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ABSTRACT

"Ensemble requirements" in surface chemistry refer to the number and shape of contiguous empty sites necessary for chemisorption of a particular molecule. Ensemble effects can play a major role in directing the course of surface reactions, leading, for example, to dramatic changes in catalytic selectivity when the active metal component is diluted upon alloying with an inert metal. We will review here fundamental surface science studies that have attempted to probe this site size requirement by diluting active sites on a single crystal surface with an inert metal overlayer. In these studies, initial sticking probability and saturation coverage are measured as a function of diluent metal coverage. We will emphasize recent results in our lab on the interaction of simple molecules (CO , H_2 , O_2) with Cu-, Ag-, and Bi-dosed Pt(111). These show that the Group IB Metals (Cu, Ag, Au) are poor diluents since they cluster into two-dimensional islands. We find that adsorbed Bi spreads out uniformly over the surface and effectively tests ensemble sizes. Theoretical models based upon Monte-Carlo simulations will be summarized which, when compared to such data, allow more accurate determination of ensemble sizes. These models predict uptake curves that deviate strongly from the commonly used $(1-\theta)^A$ law (A = number of sites in ensemble), which is valid only for an array of isolated ensembles.

I. INTRODUCTION

An ensemble requirement refers to the size and shape of sites that are necessary for chemisorption or a reaction step at a surface. In a Langmuir-like adsorption model, for example, the rate of adsorption may be expressed as $(1-\theta_A^*)^A$, where θ_A^* refers to the coverage or the fraction of occupied sites, and A refers to the number of contiguous free sites, or the ensemble size, required for that adsorbate.

In hydrocarbon reactions for the petroleum industry, the selectivity of certain catalysts has been tuned by controlling the number of contiguous sites available on the surface [1-4]. This can be done by decreasing the particle size of a supported metal down to clusters of a few atoms [4] or by diluting the active metal with the addition of a second, inert metal such as Au [1-4]. For example, selectivity to dehydrogenation over hydrogenolysis of hydrocarbons can be increased by diluting Ni, Ru, or Os catalysts with Cu [1-4]. This has been explained in terms of an ensemble effect, whereby hydrogenolysis reactions require a larger group of active metal atoms to accommodate the fragments resulting from C-C bond cleavage. Only C-H bonds are broken in dehydrogenation reactions. Many other examples have been mentioned in recent excellent reviews [1-4]. Thus, there is a strong practical motivation for developing a fundamental understanding of ensemble effects in surface reactions.

One of the most important barriers in understanding ensemble effects involves successfully determining the ensemble size requirement for an overall reaction and for its individual steps, such as chemisorption. In fact, matching the ensemble size for the overall catalytic reaction with the size required

for individual steps could be an elegant method for specifying the rate-determining step in a reaction mechanism. Most results to date have been obtained by masking sites of the active metal with inert species, and observing the resulting effects on adsorption and reactions with the molecule of interest [5-20]. Early work along these lines has used bulk alloys of the active metal and a second, inert metal [5-8,16,17]. For detailed understanding, surface analysis is absolutely required here, since the surface composition of the alloy rarely reflects that of the bulk [3-4,7]. Another convenient method involves vapor-depositing an inert species, such as Au, Ag, or Cu, onto the surface of the active metal. Here, the whole range of surface compositions is easily attained in a well-characterized way. Recently, much work has appeared using this method [9-15,18-20]. It is important to choose the masking atom so that its electronegativity matches that of the active metal, to minimize electronic effects. We have recently found one of the major shortcomings of this technique: the Group IB metals tend to show attractive lateral interactions, coalescing into two-dimensional islands on the surface [19-21]. It unfortunately leaves large regions essentially free of the blocking agent, and the reaction rate or the adsorbate coverage falls only linearly with the coverage of the masking agent (Au, Ag, or Cu) [12-15,18-20]. This can easily be misinterpreted as indicating an ensemble size of one site for the reaction of interest.

Another problem that has persisted in studying ensemble sizes in this way is the lack of a good theoretical formalism with which to match the data. Even if the masking atoms were distributed randomly on the surface, data to date

[5-21] have almost exclusively been modeled assuming completely isolated (non-overlapping) ensembles of sites for the adsorbate and a random distribution of the masking agent, which blocks only one site. This leads to an expression [5,6,16,21,22] where the initial sticking probability (S_1) or saturation coverage (θ_A^{sat}) of the adsorbate molecule varies with inert metal coverage as:

$$S_1 \text{ or } \theta_A^{sat} = (1 - \theta_M^*)^A \quad (1)$$

Here, θ_M^* is the fractional coverage of the inert, masking atom and A is the number of contiguous sites (ensemble) required for adsorption of the molecule of interest.

In reality, for $A > 1$ the adsorbate sites can overlap and do, so that Eq. (1) is significantly in error for large A. In an early work, Herington and Rideal [22] recognized this difficulty and performed a few simple Monte-Carlo calculations that eliminated this assumption of overlapping sites. Their results indicated that, indeed, Eq. (1) is greatly in error for large A. Unfortunately, that work has been largely ignored until now.

In this paper we will review results of our recent, accurate Monte Carlo calculations, where the adsorbate sites are allowed to fully overlap, and the adsorbed molecules are allowed to migrate and re-orient on the surface. A complete presentation of these results will appear elsewhere [23], where a large range of possible geometries are examined. We will also compare these calculations with experimental results [19-21,24] for the adsorption of CO, H₂,

and O_2 on Ag, Cu, and Bi-masked Pt(111) surfaces. This comparison has allowed a determination of the ensemble size required for adsorption, as well as the size of the ensemble that is masked by each Bi atom. Bismuth is shown to be preferable to the Group IB elements as a masking agent, since it shows weakly repulsive lateral interactions and therefore tends to spread uniformly across the surface.

II. EXPERIMENTAL

Preparation and cleaning of the Pt(111) single-crystal are described in a previous publication [19]. The Bi vapor-deposition technique and experimental arrangement are also described therein [21]. Auger electron spectroscopy, low-energy electron diffraction (LEED), and thermal desorption mass spectroscopy (TDMS) were conducted using conventional apparatus [19,21].

III. THEORY

The Monte Carlo simulations were carried out on both square and hexagonal lattices, using a 58×58 grid of binding sites. To eliminate edge effects, all properties were computed from a 50×50 grid centered within the 58×58 lattice. A case was defined by choosing the lattice type, a size (M = number of binding sites) and shape (configuration of binding sites) for the masking agent, and a size (A) and shape for the adsorbate molecule. Note that for some shapes, more than one orientation is possible. For each case, the saturation coverage of the adsorbate with no diffusion allowed ($\nu_{A,nd}^{sat}$), the saturation coverage allowing adsorbate diffusion ($\theta_{A,d}^{sat}$), and the initial sticking probability (S_1) were determined as a function of the pre-coverage of the masking

molecules (θ_M). To obtain these values with statistical error bars ($<0.1\%$), 100 independent Monte Carlo simulations were performed for each value of θ_M . The following describes the procedure for one such simulation.

The first stage consists of spraying down a coverage θ_M of immobile masking agent. This is accomplished by repeatedly choosing a random position and orientation on the grid until the desired number of mask agents is generated. Each time this location overlaps an existing mask agent, the choice is discarded. (Two species "overlap" if they share one or more binding sites.) Note that the maximum value of θ_M that can be achieved in this manner is less than one, unless the mask agent uses only one binding site.

The initial sticking probability for this θ_M is determined by repeatedly attempting to place an adsorbate in a random position and orientation on the masked lattice, removing the adsorbate molecule before the next attempt. S_1 is computed as the fraction of attempts that lead to no overlap with mask agents.

To determine $\theta_{A,nd}^{sat}$, adsorbate molecules are sprayed down randomly, allowing each new adsorbate to "stick" only if it overlaps no existing mask or adsorbate. This is continued until there are no more "holes" that can fit an adsorbate molecule. (Hereafter, this is the definition of a hole.)

Starting from a configuration in which all holes have been filled, the value for $\theta_{A,d}^{sat}$ is determined by allowing the adsorbate molecules to diffuse, and filling any new holes that open up. An attempted diffusion move consists of selecting, at random, an existing adsorbate molecule, a displacement, and a new orientation. If placing the adsorbate in this new position causes no overlap with another molecule, the move is accepted. The immediate region is then searched for holes, which, if found, are filled with a new adsorbate molecule.

There is no need to search for a hole if the move is rejected. The maximum distance and direction of an attempted move is limited only by the size of the molecule. Since all holes are filled as they are created, moves that lead to no overlap between the old adsorbate position and the new adsorbate position need not be attempted. The diffusive moves are repeated until $N_{\max}$ successful moves are carried out without a new hole being filled. In the present study, $N_{\max}$ was taken as twenty times the number of possible moves of the system (each time a hole was filled the number of possible moves of the system was recomputed using a systematic scan). This is by far the most time-consuming stage of the simulation.

Based on tests varying the lattice size and the convergence criteria, these calculations appear to be accurate to within a few percent. Full details are presented elsewhere [23].

Coverages (θ) here are defined such that $\theta = 1$ corresponds to one per surface site. Thus, the maximum possible coverages are $\theta_A = 1/A$ and $\theta_M = 1/M$; and, $\theta_M^* = M\theta_M$.

IV. GENERAL THEORETICAL RESULTS

Example results for a hexagonal lattice of sites are shown in Figs. 1 and 2, for an adsorbate requiring seven sites ($N = 7$) and for masking agent sizes (M) of one and seven, respectively. If $M = 1$, the initial sticking probability is rigorously given by the $(1 - M\theta_M)^7$ expression of Eq. (1). However, the true saturation adsorbate coverages $\theta_{A,d}^{\text{sat}}$ and $\theta_{A,nd}^{\text{sat}}$ disagree with this expression by up to a factor of three in initial slope. Remember that Eq. (1) predicts θ_A^{sat} under the assumptions of isolated ensembles for the adsorbate and a random

distribution of singly masked sites. This disagreement with our results shows the error in these assumptions. When M is large, errors as large as a factor of two result in the initial sticking probability as well, with even larger errors for θ_A^{sat} . Thus, the assumptions of Eq. (1) would lead one to extract ensemble sizes too small by a factor of two to three, depending upon whether one was fitting data for S_1 or θ_A^{sat} . The error in S_1 results solely from the assumption that the masking agent randomly blocks single sites, and not ensembles of contiguous sites.

Results of the type shown in Figs. 1 and 2 have been computed for hexagonal lattices for $A = 1$ to 7 and $M = 1$ to 7 and for square lattices for $A = 1$ to 5 and $M = 1$ to 5. These results, which will be presented in detail elsewhere [23], show the same trends as above and allow the following further general conclusions to be drawn.

(1) When attempting to determine ensemble sizes, choosing a masking agent as small as possible provides the greatest distinction between ensemble requirements. This will also be true in tuning selectivity of catalysts by this masking method. Essentially, finite ensemble sizes for the mask ($M > 1$) resemble islands of single-site masking agents, and in the limit of large M , no distinction between A values would appear.

(2) Fitting S_1 data distinguishes ensemble sizes more readily than θ_A^{sat} data (see caveat below).

(3) For $A > 1$, $\theta_{A,\text{nd}}^{\text{sat}}$ is always less than unity even when $\theta_M = 0$, due to random generation of free ensembles too small for the adsorbate. This point has been noted before [22,25-26].

(4) The saturation coverage with diffusion always has a steeper initial slope than without diffusion, although the curves get very close when $M\theta_M \geq 0.4$. Neither drops as steeply as the prediction of Eq. (1).

(5) Down to very low values of $\theta_{A,nd}^{sat} (\leq 0.2)$, this curve is almost linear even for large A, in distinct contrast to the curvature of Eq. (1). This was noted previously [22,25].

(6) Eq. (1) is only valid for θ_A^{sat} when $A = 1$.

V. EXPERIMENTAL RESULTS

We have recently shown [21,24] that the submonolayer growth mode of Bi on Pt(111) results in hexagonal overlayer structures with Bi adatoms maximizing their nearest neighbor distances due to lateral repulsive forces. Briefly summarizing, Bi deposition at -600 K is observed by LEED to produce in succession $p(2 \times 2)$, $(\sqrt{3} \times \sqrt{3})R30^\circ$, $p(3 \times 3)$ and $p(4 \times 4)$ patterns consistent with proposed models [21,24] giving ideal coverages (θ_{Bi}) of 0.25, 0.33, 0.44, and 0.56, respectively. The $p(4 \times 4)$ pattern at $\theta_{Bi} = 0.56$ corresponds to a close-packed Bi overlayer. Below $\theta_{Bi} = 0.25$ no LEED features are seen and therefore Bi may be randomly dispersed on the Pt(111) surface. For coverages greater than 0.56, three dimensional islands begin to form. It is difficult to tell if these islands are pure Bi or Bi/Pt alloys, as they cover a small fraction of the surface [24]. A more exhaustive description of the growth modes, as well as their variation with temperature, is contained in our recent results [21, 24]. The submonolayer growth mode behavior for Bi/Pt(111) is to be contrasted with the growth mode behavior exhibited by Group IB transition metals (Cu, Ag,

Au) on Pt(111), namely, large two-dimensional island formation in the submonolayer region [15,18-20]. This difference makes Bi a much better choice as a masking agent for testing ensemble sizes, as described below.

In Fig. 3a the integrated thermal desorption spectra for saturation exposures of CO and H₂ are shown plotted as a function of Bi, Cu, and Ag precoverage. The saturation CO exposure at 275 K was shown to produce a c(4 x 2) pattern on the clean Pt(111) surface consistent with $\theta_{\text{CO}}^{\text{sat}} = 0.5$ [27-26]. The H₂ TDMS for a saturation exposure at 150 K on clean Pt(11) was in good agreement with literature data [27-28]. Saturation exposure of H₂ gives 0.8 H-adatoms per Pt surface atom [29], with p(1x1) filling of three-fold hollow sites [30].

For Ag and Cu, both CO and H₂ are blocked in a one-to-one fashion, consistent with the two-dimensional islanding of Ag and Cu [19-20]. For the Bi modified surfaces the attenuation in the uptake of H₂ is notably different from that seen for CO and reflects the different ensemble sizes involved. The solid lines in Fig. 3a represent our Monte Carlo calculations for saturation coverage allowing surface diffusion for the cases: a) M = 4, A = 2; b) M = 4, A = 1; and c) M = 2, A = 2.

In Fig. 3b the amount of molecularly adsorbed O₂ for a saturation exposure at 110 K is shown plotted versus Bi precoverage. The amount of molecularly adsorbed O₂ was determined by summing the integrated TDMS (M/e = 32) traces for the desorption of molecular O₂ occurring at 150 K and for the desorption of O₂ from the atomic state at ~700 K [21]. The atomically adsorbed oxygen results from dissociation of that fraction of molecular oxygen that does not desorb and has been shown [31] to occur only upon heating the sample above ~150 K. Thus,

the coverage of oxygen we plot here reflects only molecularly adsorbed O_2 at 110 K. For clean Pt(111), the saturation coverage of $O_{2,a}$ is 0.4 molecules per Pt surface atom [31].

Full details of the interactions of CO, H_2 and O_2 with Bi/Pt(111) will appear elsewhere [21,24].

VI. DISCUSSION

The theoretical models shown in Fig. 3 provide a good fit to the experimental data at low Bi coverage for molecular CO, dissociative H_2 and molecular O_2 adsorption on Pt(111). These models assume ensemble sizes for the adsorbate of two, one, and two sites, respectively, which is consistent with the saturation coverages of these species (0.5 [27-28], 0.8 [29], and 0.4 [31]). It is further assumed that each Bi adatom blocks two such sites for CO_a and four such sites for H_a and $O_{2,a}$. We also allow CO_a and $O_{2,a}$ to diffuse, although the differences are almost undistinguishable if diffusion is disallowed. (When $A = 1$, there is no difference.) As can be seen in Fig. 3, there is almost no distinction between the $A = 1$ and $A = 2$ models when $M = 4$, so that our data cannot actually distinguish these ensemble sizes. This emphasizes the desirability of choosing small M . Finding a masking agent with $M = 1$ and no electronic ligand effects is a challenge to surface science.

The data for $O_{2,a}$ and H_a in Fig. 3 would have been equally well modeled using $A = M = 3$ (with diffusion). We have rejected such models since the saturation coverages of these species on clean Pt(111) indicate ensemble sizes $A = 2$ and 1, respectively, and not 3. An important point here is that either suitable theoretical model differs significantly from that predicted by Eq. (1), which would require $A = M = 2$. In this case, the error appears as a

factor of two in M , the ensemble masked by Bi, but for large adsorbates the error would appear in the value of A . In understanding bimetallic catalysts, both values are equally important.

An important point indicated by these results is that a given masking agent can poison a different number of sites depending upon the adsorbate (or reaction) of interest: $M = 2$ for CO_a and 4 for H_a and $\text{O}_{2,a}$. How this can arise is indicated by the insert of Fig. 3b. A lattice of Pt-size "sites" are shown by hollow spheres ($r = 1.39 \text{ \AA}$) and the Bi adatom by a larger filled sphere ($r = 1.84 \text{ \AA}$ [32]). The location of the "sites" is not necessarily "a-top"; and this lattice could be translated across the Pt(111) lattice to place the "sites" in any arbitrary location. For the Bi location as shown, two sites will clearly be blocked for all adsorbates. However, two other sites are only slightly covered, so that they may or may not be masked, depending upon the adsorbate.

The nonlinearity in the data of Fig. 3 for larger θ_{Bi} is not fit by the theoretical models we have used, and in general occurs for ideal cases in θ_A^{sat} only for very large A [23]. We feel that the nonlinearity occurs here because of the fact that Bi adatoms change their location as coverage grows, consistent with our structural models based on LEED data [21,24]. Note that the saturation Bi coverage is 0.56 [21], so that each Bi atom only blocks about two sites for its own adsorption. Further nonlinearity arises from nonhomogeneous Bi coverage across the surface [24], and from the fact that multilayer Bi growth already begins by $\theta_{\text{Bi}} \geq 0.25$ [24]. For these reasons, it is advised to fit data only at low θ_M (initial slope) in determining ensemble sizes. Also, in this low coverage range, the assumption of randomness is most valid.

We noted in Section III that for the ideal case, fitting S_1 data provides the greatest distinction between adsorbate sizes. However, a strong warning is advised here! If the impinging gas molecule, upon hitting a masking atom, is able to deflect into a free site or enter a weakly bound precursor state in which it can diffuse to find a free site, the theory here is invalid. Determining the extent of such phenomena is almost impossible except when the precursor state is so long-lived that S_1 mimics θ_A^{sat} . Thus, it is advised to model θ_A^{sat} data, which is more easily obtained anyway.

Determining whether diffusion can or cannot occur may be difficult for a given adsorbate. Using the highest temperature before desorption or dissociation occurs is advised. Fortunately, the ensemble size for an adsorbate found from its absolute saturation coverage on a clean surface will only agree with that found using the masking technique for large A if the proper assumption about diffusion is used. For example, if diffusion were disallowed the data would actually obey the curve for $\theta_{A,nd}^{sat}$ of Fig. 1 ($M = 1$, $A = 7$). Falsely assuming that diffusion were allowed would lead to values of $A = 4$ and 10.5 by the two methods. Thus, comparing the two methods allows accurate determination of both the ensemble size and the participation of diffusion by the adsorbate.

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FIGURE CAPTIONS

Figure 1. The saturation coverage with surface diffusion (θ_a^{sat}), and the initial sticking probability (S_i) determined from Monte Carlo calculations for the masking agent requiring 1 site ($M=1$) and adsorbate requiring 7 sites ($A=7$). The predictions for S_i and θ_A^{sat} assuming isolated ensembles of sites (Eq. 1) is also shown.

Figure 2. Same as Fig. 1, only $M=A=7$.

Figure 3. (A) Saturation coverages of dissociatively adsorbed hydrogen and molecularly adsorbed CO as a function of metal precoverage. The data from the Bi/Pt(111) interface are shown as actual points. The generalized result for Ag or Cu on Pt(111) is shown as a dashed line. Hydrogen was dosed at 150 K and carbon monoxide at 275 K. The solid lines are the theoretical curves computed as described in text for cases; (a) $A=2, M=4$; (b) $A=1, M=4$; and (c) $A=2, M=2$. (B) Saturation coverage of molecularly adsorbed O_2 on Pt(111) as a function of Bi precoverage. The solid line (d) is the theoretical curve for the case $A=2, M=4$. O_2 was dosed at 110 K. Inset: a lattice of Pt-sized sites with a single Bi adatom, showing how it could block two or four sites, depending upon the nature of the adsorbate.

Fig. 1

Fig. 2

Fig. 3