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Optimal Structure of Bimetallic Catalysts for the \( A + B \) Reaction

A. P. J. Jansen and C. G. M. Hermse

Schuit Institute of Catalysis, T/SKA, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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We have determined the most reactive structures of a bimetallic catalyst for the \( A + B \) reaction when \( A \) adsorbs on one component of the catalyst and \( B \) on the other. We show that there are various structures that can become the most reactive depending on the reaction rate constants. The reactive structure can be predicted without any calculations or simulations in some limiting cases, but in general this is not possible. In general a balance has to be found between maximizing the rate of \( AB \) formation, by maximizing the length of the interface between the components, and maximizing the number of sites for the adsorbate that adsorbs more slowly. Diffusion has a major effect on what is the most reactive structure.

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On a catalyst with a uniform surface the reactants often compete for the same sites, and it may happen that the stronger adsorbing reactant occupies all sites and poisons the catalyst. In simulations of CO oxidation, for example, CO poisoning already occurs at CO-O\(_2\) gas ratios much below the stoichiometric ratio, and the maximum attainable reactivity is quite low as a consequence [1]. In a bimetallic catalyst this can be avoided; one reactant adsorbs on one component and the other reactant on the other [2]. The reactivity of the bimetallic catalyst can then become much higher than each of the separate components (synergistic effect). We have recently studied CO electro-oxidation on a Pt-Ru catalyst [3]. In this system CO preferably adsorbs on Pt sites and water dissociatively adsorbs on Ru sites. The CO\(_2\) formation takes place mainly at the Pt-Ru interface. As a consequence small Pt and Ru islands give a more reactive catalyst than large islands, because small islands have a longer Pt-Ru interface.

Supported metal catalysts can also avoid poisoning. The support may function as a reservoir of reactants which diffuse to the metal where they react (spillover effect) [4–7]. It is also possible that the metal has two (or more) facets with different adsorption characteristics; at reaction conditions in which one would be poisoned, the other might be reactive [6,8]. The communication between metal and support or between different facets of the metal leads in general to very different kinetics from the kinetics of the separate parts.

Preparation methods for catalysts have become so sophisticated that sometimes the structure of a catalyst can be controlled down to the atomic scale [9,10]. This naturally raises the question what the structure is of the ideal catalyst. In this paper we determine for a simple model of a bimetallic catalyst what structure is optimal; i.e., what structure has the highest reactivity. It turns out that a maximum interface does not lead in general to an optimal catalyst. We show that there are limiting cases for which one can say in advance what the optimal structure is, but even for this simple model there can be a large number of structures that may be optimal depending on the rate constants.

Our model is a simplification of the model for the CO electro-oxidation on Pt-Ru mentioned above. It consists of a square grid of sites that are of two types, which we call \( \alpha \) and \( \beta \). We have the following reactions.

\[
A(\text{gas}) + \ast\alpha \rightarrow A(\text{ads}), \tag{1}
\]

\[
B(\text{gas}) + \ast\beta \rightarrow B(\text{ads}), \tag{2}
\]

\[
A(\text{ads}) + B(\text{ads}) \rightarrow AB(\text{gas}) + \ast\alpha + \ast\beta. \tag{3}
\]

Here \( \ast\alpha \ (\ast\beta) \) stands for a vacant \( \alpha \) (\( \beta \)) site. In the last reaction \( A \) and \( B \) must be nearest neighbors. This model is equivalent to the model of CO electro-oxidation on a Pt-Ru surface at an intermediate overpotential; \( A \) is CO, \( B \) is OH after adsorption and H\(_2\)O before, \( \alpha \) is a Pt site, and \( \beta \) is a Ru site. We have maximized the synergistic effect as a surface of only \( \alpha \) or only \( \beta \) sites shows no reactivity at all. Most of the results we will present hold for the low temperature situation where there is little or no diffusion of the adsorbates. We will, however, also comment on how our results change when the adsorbates diffuse. This model has been studied extensively for the case with just one type of site onto which both adsorbates can adsorb. The competition for the sites leads to two poisoned states with the catalyst being completely covered by either \( A \) or \( B \) [11,12]. There have been, of course, many studies in which the reactivities of different bimetallic catalysts have been compared, but we have been able to find just two (theoretical) studies with a search for the absolutely most reactive structures. One deals with an \( A + B_2 \) model (CO oxidation) [2], and the other with our \( A + B \), but with infinitely fast \( AB \) formation [13]. In that study a genetic algorithm was used to determine the optimal structures; two of which were found. We will show here that there are at least three more.

We have simulated the model above with dynamic Monte Carlo (DMC) based on a master equation [14–16]. The rate constants of the reactions as they appear in the master equation are \( W_{A,\text{ads}}, W_{B,\text{ads}}, \) and \( W_{\text{rx}} \). Periodic boundary conditions were used, and the sizes of the grids were \( 63 \times 63, 64 \times 64, \) and \( 65 \times 65 \) depending on the size of the unit cell of the surface. The program CARLOS...
with the variable step size method was used to generate all the reactions and their times that occur in the system [17,18]. The mean field approximation was also used to get a crude idea of the reactivity of different surface structures. As mean field (MF) holds only for randomized systems, it is often assumed that it cannot be used for ordered bimetallic systems. This assumption is invalid when the \( \alpha \) and \( \beta \) sites are treated separately, which then leads to the following equations.

\[
\frac{d\theta_A}{dt} = W_{A,\text{ads}}(1 - \theta_A) - N_{\beta}W_{rx}\theta_A\theta_B, \quad (4)
\]

\[
\frac{d\theta_B}{dt} = W_{B,\text{ads}}(1 - \theta_B) - N_{\alpha}\theta_BW_{rx}\theta_A\theta_B. \quad (5)
\]

Here \( \theta_A (\theta_B) \) is the coverage of \( A (B) \) normalized with respect to the number of \( \alpha (\beta) \) sites. \( N_{\beta} (N_{\alpha}\beta) \) is a structure factor that stands for the average number of \( \beta (\alpha) \) neighbors of an \( \alpha (\beta) \) site. One expects these equations to give good results if the \( AB \) formation is slow, but there will be deviations if the \( AB \) formation is fast.

Figure 1 shows the optimal structures as a function of the rate constants. The behavior of the system depends on just the two parameters \( W_{A,\text{ads}}/W_{rx} \) and \( W_{B,\text{ads}}/W_{rx} \), instead of on all three rate constants. All the optimal structures in Fig. 1 are what we call regular structures. In these structures each \( \alpha \) site has the same number of \( \beta \) neighbors, and each \( \beta \) site has the same number of \( \alpha \) neighbors. Our DMC simulations have yielded no optimal nonregular structures. The rationale of why all optimal structures are regular is the following. A nonregular structure will have \( \alpha \) (or \( \beta \)) sites with different numbers of \( \beta \) neighbors. Consequently, the \( \alpha \) sites will show different reactivities, and it is better to change the structure so that the number of \( \beta \) neighbors of the less reactive \( \alpha \) sites equals the number of \( \beta \) neighbors of the more reactive \( \alpha \) sites. This then leads to a regular structure.

As the number of \( \beta \) neighbors of the \( \alpha \) sites and the number of \( \alpha \) neighbors of the \( \beta \) sites can vary from 0 to 4, there can maximally be 25 different structures. Each \( \alpha \) site must, however, have at least one \( \beta \) neighbor and vice versa, or a structure with only \( \alpha \) or only \( \beta \) sites is obtained. This leaves at most 16 interesting regular structures. If we interchange the values of \( W_{A,\text{ads}} \) and \( W_{B,\text{ads}} \), and at the same time replace all \( \alpha \) sites by \( \beta \) sites and all \( \beta \) sites by \( \alpha \) sites, then we have essentially the same situation with the roles of \( A \) and \( B \) reversed. Of the 16 regular structures then only 10 need to be investigated. Without loss of generality we can restrict ourselves to regular structures with \( \alpha \) sites that have at least as many \( \beta \) neighbors as \( \beta \) sites have \( \alpha \) neighbors.

If \( N_{\alpha} (N_{\beta}) \) is the number of \( \alpha (\beta) \) sites, then we have

\[
N_{\alpha}N_{\beta}\alpha = N_{\beta}N_{\alpha}\beta, \quad (6)
\]

![Image](image.png)

FIG. 1. Surface structures and the values of the rate constants for which they are the most reactive. The solid (open) circles indicate \( \alpha (\beta) \) sites. The squares and rectangles indicate unit cells. The \((2\sqrt{2} \times 2\sqrt{2})R45^\circ-2\alpha + 6\beta\) structure is a representative of an infinite set of structures (see Fig. 2). The region where they are the most reactive structures is very thin; it is only visible as a thickening of the curve separating the \((3\sqrt{2} \times \sqrt{2})R45^\circ-\alpha + 2\beta\) and \((\sqrt{5} \times \sqrt{5})R26.6^\circ-\alpha + 4\beta\) structures for \( W_{A,\text{ads}}/W_{rx} < 0.19 \). The number of \( AB \)s formed per site and per unit time for each structure in this figure is about 25% to 50% higher than for a structure with the same fractions of \( \alpha \) and \( \beta \) sites, but with a random distribution of the sites.
as left- and right-hand sides are equal to the number of \( \alpha \)-\( \beta \) pairs. For adsorption different regular structures with \( N_{B_1} = N_{B_2} \) are the same, because \( N_\alpha = N_\beta \), but the formation of \( AB \) is, of course, faster when \( N_{B_1} = N_{B_2} \) becomes larger. This means that when \( N_\alpha = N_\beta \) the problem with \( N_{B_1} = N_{B_2} = 3 \) can be optimal. This is nothing but the checkerboard structure \( (\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \). Similarly, comparing \( N_{B_1} = 2 \) and \( N_{B_2} = 1 \) with \( N_{B_1} = 3 \) and \( N_{B_2} = 2 \) shows that only the latter combination can be optimal.

Finally, there is no regular structure with \( N_{B_1} = 4 \) and \( N_{B_2} = 3 \). This means that only the five regular structures with \( (N_{B_1}, N_{B_2}) = (4, 4), (4, 2), (4, 1), (3, 2), \) and \( (3, 3) \) need to be investigated. Indeed, Fig. 1 shows that for each of these structures there is a set of rate constants for which the corresponding structure is the most reactive one. They are all found for \( W_{B_\text{ads}} \leq W_{A_\text{ads}} \). For \( W_{B_\text{ads}} > W_{A_\text{ads}} \) we find the same structures with the \( \alpha \) sites replaced by \( \beta \) sites and vice versa. In the following we will restrict ourselves to \( W_{B_\text{ads}} \leq W_{A_\text{ads}} \).

If \( W_{B_\text{ads}} = W_{A_\text{ads}} \) it is clear why the checkerboard structure is the most reactive one. The number of \( \alpha \) and the number of \( \beta \) sites should be equal, and the checkerboard structure has the maximum number of \( \alpha \)-\( \beta \) pairs.

When \( W_{B_\text{ads}} \) and \( W_{B_\text{ads}} \) differ by not too much, it seems clear that maximizing the number of \( \alpha \)-\( \beta \) pairs will yield the optimal structure. When \( W_{B_\text{ads}} \) becomes smaller, this will become more important. In the limit \( W_{B_\text{ads}} \rightarrow 0 \) the checkerboard structure will be the most reactive for all finite values of \( W_{A_\text{ads}} \) and \( W_{B_\text{ads}} \). This is why the boundary between the checkerboard and the \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) structure has a slope that goes to zero for \( W_{A_\text{ads}} / W_{B_\text{ads}} \rightarrow \infty \).

It is also understandable why the \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 2\beta \) structure is the most reactive one when \( W_{B_\text{ads}} \ll W_{A_\text{ads}} \). One wants as many \( \beta \) sites as possible to get Bs on the surface, but \( \beta \) sites without \( \alpha \) neighbors should be avoided, as they are unreactive. Equation (6) leads then to \( N_{B_1} = 4 \) and \( N_{B_2} = 1 \), which can only be realized with the \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 4\beta \) structure. The rate constant for the AB formation should not be too small, as otherwise it will be more important to increase the number of \( \alpha \)-\( \beta \) pairs.

It may be clear why the checkerboard and the \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 4\beta \) structures are found in the limiting cases, but it is less clear why other structures are more reactive for some combination of rate constants. For large \( W_{A_\text{ads}} / W_{B_\text{ads}} \) we see that a \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) structure may be optimal. This structure is a compromise between having more \( \beta \) than \( \alpha \) sites, and a maximum number of \( \alpha \)-\( \beta \) pairs. The \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) structure has twice as many \( \beta \) as \( \alpha \) sites, whereas for the \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 4\beta \) structure the ratio is four to one, and for the checkerboard structure there are as many \( \beta \) as \( \alpha \) sites. In all three structures the \( \alpha \) sites have four \( \beta \) neighbors, but the \( \beta \) sites have four, two, and one \( \alpha \) neighbor for the checkerboard, the \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \), and the \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 4\beta \) structure, respectively.

For \( W_{A_\text{ads}} / W_{R} \rightarrow \infty \) the checkerboard and the \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) structures are equally reactive when \( W_{B_\text{ads}} / W_{R} = 2 \). This can be understood as follows. Because A adsorption is fast, the \( \alpha \) sites are always occupied. It then takes a time \( 1 / W_{B_\text{ads}} \) for a vacant \( \beta \) site to become occupied, and a time \( 1 / (N_{B_1} / W_{R}) \) to become vacant again. The number of reactions per \( \beta \) site per unit time is then \( N_{B_1} / W_{A_\text{ads}} / (W_{B_\text{ads}} + W_{B_\text{ads}} / W_{R}) \). The number of reactions per site (\( \alpha \) or \( \beta \)) per unit time is then \( N_{B_1} / W_{A_\text{ads}} / [(N_\alpha + N_\beta) (W_{B_\text{ads}} + N_{B_1} / W_{R})] \). This value is the same for the checkerboard and the \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) structure if \( W_{B_\text{ads}} / W_{R} = 2 \). Similarly, we find that for \( W_{A_\text{ads}} / W_{R} \rightarrow \infty \) the structures \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) and \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 4\beta \) are equally reactive if \( W_{B_\text{ads}} / W_{R} = 1 / 2 \).

If the \( AB \) formation is much faster than the adsorptions, then the number of \( \alpha \)-\( \beta \) pairs is less important than an optimal ratio of \( \alpha \) and \( \beta \) sites. As a consequence there are two more optimal structures for small \( W_{B_\text{ads}} / W_{R} \) and \( W_{B_\text{ads}} \leq W_{A_\text{ads}} \): both, however, are on the most reactive structure in a very narrow strip of rate constants. The \( (\sqrt{5} \times \sqrt{5})R26.6^\circ - \alpha + 2\beta \) structure has less \( \alpha \)-\( \beta \) pairs than its neighboring structures in Fig. 1, but the ratio of the number of \( \alpha \) and \( \beta \) sites is in between the ones of the checkerboard and the \( (3\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 2\beta \) structure. The same holds for the \( (2\sqrt{2} \times \sqrt{2})R45^\circ - \alpha + 6\beta \) structure.

Remarkably the \( (2\sqrt{2} \times 2\sqrt{2})R45^\circ - \alpha + 6\beta \) structure is just one representative of an infinite set of structures that all have the same reactivity according to our DMC simulations. In all these structures all sites have one \( \alpha \) and three \( \beta \) neighbors. The \( (2\sqrt{2} \times 2\sqrt{2})R45^\circ - \alpha + 6\beta \) structure has the smallest possible unit cell. The \( (2\sqrt{2} \times 4\sqrt{2})-2\alpha + 6\beta \) structure is the other structure that we have found with a smallest possible unit cell. Structures with larger unit cells are also possible, and there are also structures with a periodicity in only one direction, or no periodicity at all (see Fig. 2).

The situation discussed above applies mainly to low temperatures as, for example, in electrocatalysis. When the temperature is high, one or both adsorbates may diffuse. An important change is that structures with \( \alpha \) (or \( \beta \)) sites having different numbers of \( \beta \) (or \( \alpha \)) neighbors may be the most reactive. In particular, an \( \alpha \) (or \( \beta \)) site with only \( \alpha \) (or \( \beta \)) neighbors will no longer be unreactive. So if \( B \) adsorption is much slower than \( A \) adsorption the most reactive structure may be one with very few \( \alpha \) sites and very many \( \beta \) sites, because it may be more important to get enough Bs on the surface than to have many \( \alpha \)-\( \beta \) pairs. Once a \( B \) has adsorbed it can always diffuse to an \( \alpha \) site and react.

The only general observation that we have been able to make is when diffusion is so fast that the MF equations hold. (For the MF equations to hold fast diffusion is not
always necessary. If the $\alpha$ sites have only $\beta$ neighbors, then obviously $A$ diffusion is irrelevant. Note that we assume that there is no diffusion from $\alpha$ to $\beta$ sites or vice versa.) By allowing for nonregular structures we can vary $N_{a|\alpha}$ and $N_{a|\beta}$ continuously. It can then be shown that the most reactive structure has $N_{a|\alpha} = 4$ when $W_{\text{ads}} \geq W_{B,\text{ads}}$. The optimal value for $N_{a|\beta}$, however, changes continuously with the rate constants, and new structures will be found that are the most reactive. Figure 3, for example, shows a $(4 \times 2) - \alpha + 3 \beta$ structure with $N_{a|\beta} = 4/3$, which is the most reactive structure along a curve of rate constants. It is possible to construct a plot similar to Fig. 1 based on the MF equations, but it is not clear if MF holds for all possible structures even if diffusion is fast.

We have shown in this paper that the question of what the optimal structure is for a bimetallic or a metal-metallic oxide catalyst is far from trivial. Some structures can be predicted in advance for limiting cases, but in general simulations of the type we have used and a good model of the system are necessary. Even for the simple $A + B$ reaction at least five structures can become optimal. An ongoing study of the $A + B_2$ reaction yields more than twice this number.

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[17] CARLOS is a general-purpose program, written in C, for simulating reactions on surfaces that can be represented by regular grids; an implementation of the First-Reaction Method and the Variable Stepsize Method, written by J. J. Lukkien.