Energetics of CO-NO reactions on Pd, Cu and Pd-Cu alloys

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The bond order conservation -Morse potential (BOCMP) model has been used to investigate the CO oxidation and NO reduction reactions on Pd(111), Cu(111) and the Pd-Cu(111) alloy surfaces. The activation barriers for the several reaction steps have been calculated and the rate-limiting step has been found. In the overall scheme of NO+CO reaction, for the Pd (111) surface NO, + N, → N₂O, reaction is the rate-limiting step; while for the Cu (111) surface it is the CO, + O, → CO₂ reaction which is rate-limiting. For the Pd-Cu alloy the surface segregation has been taken into account and the role of segregation on the activation barrier of the rate-limiting step has been studied. The effect is found to be small. The activity of the Pd-Cu (111) alloy surface for the above two reactions has been calculated and the role of local environment on the reactions studied. It is found that for the NO, + N, → N₂O, reaction the active sites are the three-fold hollow sites where an adsorbed NO has three Cu atoms as nearest neighbours. For the CO, + O, → CO₂ reaction, on the other hand, the most active sites are the three-fold hollow sites with three Cu nearest neighbours, and the sites with two Cu and one Pd atom as nearest neighbours.

CO oxidation and NO reduction are the two most important reactions in controlling pollution from automobile exhaust gases. The combination of Pt and Rh on ceria is so far found to provide the most effective three-way catalyst which at a specific air-fuel ratio\textsuperscript{1,6} converts CO, NO and the unburnt hydrocarbons into harmless products. However, Rh and Pt being very costly metals, it has become imperative to find some substitute for these metals. With this aim, various combinations of metals and their alloys are being tried worldwide\textsuperscript{2,7}. Pd-Cu appears to be a good candidate for CO + NO reaction since Cu dissociates NO very efficiently\textsuperscript{8,11}, and Pd is a good oxidation catalyst. It is important, therefore, to study closely the Pd-Cu system for these reactions. It will be important also to study how far the segregation behaviour influences the rate of these reactions. In this work we have studied for the Pd-Cu system the energetics of the possible reaction steps in the overall CO + NO reactions and found out the rate-limiting step as a function of the alloy composition. The influence of segregation and the local environment on the activity of Pd-Cu surface is also studied. The details are presented below:

Methodology

\underline{Reaction steps and the activation barrier}

For the simultaneous oxidation of carbon monoxide and reduction of nitric oxide the overall reaction may be given as,

\[ \text{CO}_\text{s} + \text{NO}_\text{s} \rightarrow \text{CO}_2 + \frac{1}{2} \text{N}_2 \]

where the suffix ‘s’ denotes the components in the adsorbed phase. However, there are many intermediate steps which are important and should be considered seriously before suggesting the rate-limiting step. Shustorovich and Bell\textsuperscript{6} have considered in detail the possible steps for the overall reaction (1). However, we discuss here only the steps which are important. They are the following:

\[ \begin{align*}
\text{CO}_\text{s} \rightarrow \text{CO}, \\
\text{NO}_\text{s} \rightarrow \text{NO}, \\
\text{NO}, \rightarrow \text{N} + \text{O}, \\
\text{CO}, + \text{O} \rightarrow \text{CO}_2, \\
\text{N} + \text{N} \rightarrow \text{N}_2, \\
\text{NO}_\text{s} + \text{N} \rightarrow \text{N}_2\text{O}, \\
\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}, \\
\end{align*} \]
Table 1 — Heats of adsorption and gas phase dissociation (in kcal/mol)

<table>
<thead>
<tr>
<th>Atom/Molecule</th>
<th>D</th>
<th>Pt(III)</th>
<th>Rh (III)</th>
<th>Pd(III)</th>
<th>Cu(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-</td>
<td>116</td>
<td>116</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>85</td>
<td>102</td>
<td>87</td>
<td>103</td>
</tr>
<tr>
<td>NO</td>
<td>151</td>
<td>26</td>
<td>26</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>CO</td>
<td>257</td>
<td>32</td>
<td>32</td>
<td>34</td>
<td>12</td>
</tr>
<tr>
<td>N(_2)</td>
<td>226</td>
<td>8</td>
<td>8</td>
<td>13.4</td>
<td>10.6</td>
</tr>
<tr>
<td>O(_2)</td>
<td>119</td>
<td>15</td>
<td></td>
<td>-13.4</td>
<td>18.3</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>384</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>1.5</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>266</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The equations (2) and (3) denote the adsorption of the molecules from gas phase. They depend, at the zero coverage limit, on the sticking coefficient of the molecules on the surface, \(S^0\), the temperature and the activation energy for adsorption. At higher coverage the sticking coefficient and the activation energy for adsorption would depend on the coverage; and hence the rate of adsorption would be coverage-dependent. The sticking coefficient of CO and NO for a few metals are given below\(^5\): 

<table>
<thead>
<tr>
<th>Metal</th>
<th>S(^0)CO</th>
<th>S(^0)NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>0.3</td>
<td>10(^{-3})</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Thus, on Cu (111) the sticking coefficient for NO adsorption is three orders of magnitude smaller compared to the value for Rh. This factor significantly distinguishes the two metals in their efficiency for NO adsorption and hence NO reduction. This is because, unless the sticking coefficient is optimum the adsorption and subsequent reduction would be small.

For the reactions (4) - (8) we can calculate the activation barrier for the different metals and compare their efficiency for CO oxidation and NO reduction. From such an analysis we would be able to suggest which may be the rate-limiting step for a particular metal.

In order to estimate the activation barrier for all these steps the bond order conservation - Morse potential (BOCMP) model of Shustorovich\(^{14}\) is used as described in ref. 6. In brief, this model, used widely to study chemisorption and surface reaction\(^{14}\), is based on the following set of assumptions\(^{14}\):

1. An adsorbate (A) interacts with a metal atom (M) through a Morse potential.
2. The interaction of the adsorbate with a group of surface atoms (M\(_n\), n being the number of metal atoms on the surface) may be considered as a sum of the individual two-body interactions expressed by Morse potential, where the interaction is limited to the nearest neighbours.

3. Along a migration path leading to dissociation the total M\(_n\)-A bond order is conserved (unity).

Results

Under these assumptions it is possible to calculate empirically the heat of adsorption of an adsorbate at top site, bridge site or at the centre hollow site if the experimental value of the adsorption energy at zero coverage and the corresponding site of adsorption are known. These adsorption energies \(Q^0\) along with the gas phase dissociation energies of the adsorbed molecules predict ultimately the activation barrier for dissociation and recombination of molecules on a metal surface. In Table 1 we present the heat of adsorption of some of the atoms and molecules on Pd, Cu, Pt and Rh. These values known experimentally or calculated by BOCMP model have been used in the calculations of activation for dissociation and recombination as described in ref. 6. The values for Pt and Rh obtained from the work of Shustorovich and Bell\(^6\) are included here for comparison. The activation energies for reactions (4) - (8) are presented in Table 2.
The activation barrier for NO dissociation \( E_{\text{NO}}^* \) in the metals decreases along the series: \( \text{Pt} > \text{Pd} > \text{Rh} > \text{Cu} \). This means that NO dissociation is very fast on Cu surface than that on Rh. Furthermore, from a comparison of the heat of adsorption of NO on the metals (Table 1) with the activation barrier for NO dissociation (Table 2), it may be concluded that the NO molecule would always dissociate on the metals rather than being desorbed from the metal surfaces. This relationship remains valid at low coverages up to \( \theta = 0.25 \) as the heat of adsorption does not change much. At higher coverages the heat of adsorption decreases and the energetics then differ leading to the possibility of both the desorption and dissociation of NO possible. However, in this work we limit ourselves to the low-coverage region.

So far as NO reduction is concerned, there are two possible reaction paths:

(i) Adsorbed \( \text{N}_x \) combines with adsorbed \( \text{N}_x \) to form \( \text{N}_2 \) (known as \( \beta \cdot \text{N}_2 \)) and

(ii) adsorbed \( \text{N}_x \) combines with adsorbed \( \text{NO}_x \) to form \( \text{N}_2 \text{O}_x \), which in turn dissociates into \( \text{N}_2 \) and \( \text{O}_x \) (known as \( \delta \cdot \text{N}_2 \)).

For all the four metals under consideration the activation energy for the first process is significantly higher than that of the second process. This follows from the activation energies as shown in Table 2. Thus, production of \( \delta \cdot \text{N}_2 \) is faster than \( \beta \cdot \text{N}_2 \) production. It may also be noticed in Table 2 that the \( \text{N}_2 \text{O}_x \) formation needs activation energy; but its dissociation is spontaneous and without any activation energy. From a comparison of the activation energy for \( \text{N}_2 \text{O}_x \) formation on the four metals it may also be concluded that the activation energy is lowest for Cu.

So far as the rate-limiting step for \( \text{CO} + \text{NO} \) reaction is concerned, we find that for Pt, Rh and Cu, \( \text{CO}_x + \text{O}_x \rightarrow \text{CO}_2 \) is the rate-limiting step; while for Pd, \( \text{NO}_x + \text{N}_x \rightarrow \text{N}_2 \text{O}_x \) is the rate-limiting step. Therefore, while for Pt-Rh (111) surface \( \text{CO}_x + \text{O}_x \rightarrow \text{CO}_2 \) may be the rate-limiting step for all bulk compositions, in the case of Pd-Cu alloy the rate-limiting step may vary from the bulk Pd-rich regime to the bulk Cu-rich regime. In this context, the role of surface segregation is very important, where segregation means that the surface concentration of a metallic component of the alloy is higher than its bulk value. In the following section we discuss the surface segregation of the Pd-Cu alloy and then we show how the segregation affects the activation energy of the rate-limiting step in the NO + CO reaction.

In this work, we do not consider the \( \text{N}_2 \) production from reaction (1) for the following reason. In BOCMP model reaction (1) could be treated as a disproportionation reaction \( \text{A} + \text{BC} \rightarrow \text{AB} + \text{C} \) as a dissociation of a quasimolecule \( \text{ABC} \) (here A, B, and C may be an atom or a molecule or a radical). Because, \( \text{NO}_x \) is dissociated very fast while CO is molecularly adsorbed, the formation of a quasimolecule of NO and CO is improbable.

Finally, the activation energies for the various reactions involving CO and NO on Pt, Rh, Pd and Cu metals are calculated on the basis of a model (BOCMP model). On the other hand, experiment gives the global activation barrier or the apparent activation barrier for a reaction. Thus the theoretical and the experimental values cannot be compared in a straightforward fashion. Because, while in experiment all the steps in the CO + NO reaction [reactions (2) - (8)] may partially influence the global or the apparent activation barrier (obtained by fitting Langmuir's equation), in the model we have considered the reaction steps individually and calculated the corresponding activation energy. Nevertheless, this model calculation gives us an indication of the rate-limiting step in the overall CO + NO reaction. In Table 2, for example, we find that in the case of Pd the activation energy for \( \text{CO}_2 \) formation is 24 kcal/mol. While experimentally, the apparent activation energy for \( \text{CO}_2 \) formation is \( \approx 31.5 \text{ kcal/mol} \). In view of the discussion above, it may be concluded that the agreement is reasonable.

In order to calculate the activation barrier for the CO oxidation and NO reduction on the Pd-Cu alloy we have to take into account the surface segregation in the Pd-Cu alloy system. Once composition of the alloy surface is known it may be possible to study the rate of the above reactions as a function of the bulk alloy composition. We may also study the local environmental effect on the activity of the alloy as described below:

**Segregation and its effect on activation energy**

The accuracy of studying the reaction rate on a bimetallic alloy surface depends on our accurate knowledge of the surface composition of the alloy. In this part of our work we would use the segregation results of Rousset et al.\(^ {15} \) to predict the activ-
ity of Pd-Cu(111) alloy surface for the CO + NO reactions. This is because the model developed to predict the segregation behaviour in that work (ref. 15) is based on several modifications of the standard broken bond model. It is important to know these modifications before using the segregation results for our work. The important modifications are the following:

(i) The bond enthalpies in the bulk alloy were obtained from the bond enthalpies of pure constituent metals and the heat of mixing.

(ii) Five layers at the top were considered to have a composition different from that in the bulk. The bond enthalpies in the top layers would then be dependent on the local environment. In order to determine the effect of the local environment on the parameters like the bond enthalpies, the interatomic distance and the mixing energy, etc., it was assumed that an atom located in the ith layer may be considered as embedded in an Equivalent Medium with concentration $X_{ic}$ given by

$$X_{ic} = \frac{Z v}{Z} X_i + \frac{Z l}{Z} X_l$$

where $Z v$ is the number of vertical bonds between two adjacent layers; $Z l$ is the number of lateral bonds in each layer and $Z$ is the total coordination number. As a consequence of this approximation the pair potentials were allowed to be different from layer to layer in the surface region.

(iii) The bond energies in the surface layer were carefully evaluated taking into consideration the coordination of the surface sites. This was done by modifying the tight binding scheme in the second moment approximation in such a way as to produce correctly the site energy in the bulk, the surface energy, the monovacancy formation energy and the bond energy of metallic dimer. This approach, termed as modified tight binding (MTB) model gave the relaxation parameter by which the surface-surface and surface-bulk bond enthalpies are modified. The layer compositions were found by minimizing the free energy.

The segregation results for the Pd-Cu (111) surface are shown in Fig. 1. It may be noted that the top layer is mildly enriched in Cu. The Cu segregation effect is more prominent in the low bulk Pd concentration regime. The segregation behaviour shown in Fig. 1 was obtained from calculations done at some arbitrary concentrations and gives only a qualitative picture. Semi-quantitative results and other details may be obtained from ref. 15.

The segregation behaviour discussed above has important effects on the activation barrier for dissociation of molecules, $E^*$. In Table 2 the values of activation barrier for the reactions have been calculated on the assumption that at low coverage the atoms and molecules are chemisorbed at central hollow sites having three-fold symmetry. To find the activation barrier for dissociation in alloys we use a...
simple assumption that the activation barrier for a reaction on the alloy would be a function of the surface composition of the alloy. For the Pd-Cu alloy, for example, we may write the activation energy as

$$E_{a}^{*} = X_{i}^{*} (Pd) E_{i}^{*}(Pd) + (1 - X_{i}^{*} (Pd)) E_{i}^{*} (Cu)$$

and likewise for other systems. The above expression considers, in effect, some kind of average effect of the alloy on the activation energy for dissociation. The results for the activation barrier for CO$_2$ formation and N$_2$O formation are shown in Fig. 2. It may be mentioned that in the absence of surface segregation one could find only a linear variation of $E_{a}^{*}$ with $X$. With respect to the conclusion made earlier in this work that for pure Pd NO$_{2} + N_2$ reaction is the rate limiting step, while for pure Cu, CO$_2 + O_2$ is the rate limiting step, we can now make some additional observation. It is about the bulk Pd concentration of 80 % above which the NO$_{2} + N_2$ reaction is the rate limiting step. And below the bulk Pd concentration of 80 %, CO$_2 + O_2 \rightarrow$ CO$_2$ is the rate limiting step.

**Activity of Pd-Cu(111) surface for CO oxidation and NO reduction**

We would consider here the CO oxidation and NO reduction on Pd-Cu alloy. The activation energy for CO oxidation and N$_2$O formation (the most probable intermediate step for the N$_2$ formation) on the pure metals and the Pd-Cu alloy has already been presented in Table 2 and Fig. 2.

For the activity 'a' of a Pd-Cu catalyst for CO oxidation we may write

$$'a' = \sum_{i} A p_{i} (X) \exp (-E_{i}^{*}/RT)$$

where $A$ is a constant depending on the collision frequency of the gas-solid system; $p_{i} (X)$ is a steric factor and is a function of the surface geometry of the system. It denotes the probability of finding a chemisorbed bond with $i$ Pd and $3-i$ Cu nearest neighbours. Usually, $p_{i} (X)$ is given by the binomial distribution

$$p_{i} (X) = \frac{3!}{i! (3-i)!} X_{i}^{3} (1 - X_{i})^{3-i}$$

The number 3 comes into picture since the adatoms are assumed to occupy the centre positions (sites with three-fold symmetry in the (111) surface of fcc lattice).

$E_{i}^{*}$ in expression (11) is the activation energy for catalytically active sites with $i$ Pd and $(3-i)$ Cu atoms as nearest neighbours. In the expression (11) the activation energy $E_{i}^{*}$ for the rate-limiting step...
would be of real importance. $E^*$ for various reaction steps may be calculated for $i = 0, 1, 2$ and 3. For a reaction step involving chemisorption at a site with $i$ Pd and $(3-i)$ Pd atoms we calculate the local activation barrier as

$$E^* = [iE_{pd} + (3-i)E_{cu}^*]/3$$

The calculation of activity 'a' is then straightforward.

Now, from the several steps in the overall CO + NO reaction to produce $CO_2$ and $N_2$ we would choose the $CO_2 + O_2 \rightarrow CO_2$ and the $NO_2 + N_2 \rightarrow N_2O_2$ reactions to study the segregational and the local environmental effect on the catalytic activity of the Pd-Cu alloy since these two steps are found to be rate-limiting at different concentration regimes.

In Figs 3 and 4 we plot the activity 'a' as a function of bulk Pd concentration of Pd-Cu alloy for the $CO_2 + O_2 \rightarrow CO_2$ and the $NO_2 + N_2 \rightarrow N_2O_2$ reactions respectively. In calculating the activity we have not considered the value of the constant $A$ in the expression. Therefore, we express activity in arbitrary units. For both the reactions we have plotted the total activity and the contribution of each term of the expression (11) to the activity. A comparison of the two reactions reveals the following features:

(i) The activity for the $CO_2 + O_2 \rightarrow CO_2$ reaction is two orders of magnitude slower than the activity for the $NO_2 + N_2 \rightarrow N_2O_2$ reaction. This follows from the difference in the magnitude of activation barrier of the two reactions.

(ii) For the $CO_2 + O_2 \rightarrow CO_2$ reaction the total contribution to the activity comes mainly from the $i = 0$ term corresponding to the active sites with three Cu neighbours and from the $i = 1$ term corresponding to two copper and one Pd atom as nearest neighbour of the active site. The contributions from $i = 2$ and $i = 3$ terms are small.

(iii) On the other hand, for the $NO_2 + N_2 \rightarrow N_2O_2$ reaction the contribution to the total activity comes mainly from the $i = 0$ term (i.e., all the three nearest neighbours of the active site are copper atoms). This is because of the fact that the activation barrier for this reaction on Cu is small (12.5 kcal/mol) compared to the barrier on Pd (25.7 kcal/mol). The contributions from $i = 1$, $i = 2$ and $i = 3$ are negligible.

**Discussion**

From the results presented in the previous sections and Tables 1 and 2 it appears that Pd is as good a CO-oxidation catalyst as Pt and Rh. Though Cu has a smaller activation barrier for the $CO_2 + O_2 \rightarrow CO_2$ reaction compared to that of Pd, Pt and Rh, the sticking coefficient of $CO$ on Cu surface is small. That makes Cu not a very good CO-oxidation catalyst. So far as NO reduction is concerned, Pd is not a suitable catalyst because of higher activation barrier for $NO_2 + N_2 \rightarrow N_2O_2$ reaction. However, Rh and Cu are better reduction catalysts because of the fact that the activation barrier for CO dissociation is much less for these two metals compared to that for Pt and Pd. For Cu, furthermore, the activation barrier for $NO_2 + N_2 \rightarrow N_2O_2$ reaction is lower than that of Rh; but the sticking coefficient of NO on Cu is 1000 times less than its value for adsorption on Rh. Thus, though Cu seems to be a very good NO-reduction catalyst for its lower activation barrier value for the $NO_2 + N_2 \rightarrow N_2O_2$ reaction, this step has to compete with the NO adsorption step to make the overall NO reduction reaction effective. Thus Rh has an edge over Cu as an NO-reduction catalyst.

Segregation of Cu in Pd-Cu (111) surface has a mild effect on the activity of the alloy for both the $CO_2 + O_2 \rightarrow CO_2$ and the $NO_2 + N_2 \rightarrow N_2O_2$ reactions. For low bulk Pd concentration both the reactions show higher activity than the activity for alloy without segregation (shown by a straight line in Figs 3 and 4 between the activity at $X=0$ and $X=1.0$ points).

The model presented above has also been used for the systems where the catalysts are small bimetallic particles having diameter in the range of 2 - 5
Fig. 6 — Activity of Pd-Cu particles as a function of total number of atoms in the particle. Bulk Pd concentration is 50% (for details see text).

nm. In Fig. 5 we have shown the surface composition of a 586-atom Pd-Cu particle where the bulk Pd concentration is 50%. The results were obtained by Monte-Carlo simulation technique\textsuperscript{17}. The shaded atoms represent the Cu atoms. It may be noticed that Cu atoms occupy the corner and the edge sites of the particle. For such nanosize Pd-Cu particles the activity for CO oxidation has been calculated from Eqs. (11) - (13) and shown in Fig. 6 as a function of the total number of atoms in the particle. The results are for 50% Pd in the bulk. The activity is found to increase with increase in particle size. This is due to the fact that for larger particles more Cu atoms segregate to the surface\textsuperscript{17} which reduces the activation barrier for CO\textsubscript{2} formation. For such particles also it may be noticed that the main contribution to the total activity comes from the adsorption sites with 3 Cu nearest neighbours (n.n) and from the adsorption sites with 2 Cu and one Pd nearest neighbours.

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