Influence of particle size on catalytic activity: CO oxidation on Rh and Pd nanostructures

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Received 1 May 1998; revised 27 July 1998

Bond order conservation Morse-potential (BOCMP) model has been used to study theoretically the dependence of CO oxidation rate on the size of Rh and Pd metal particles. We assume cubo-octahedral geometry for the metal particles having 38, 201, 586, 1289 and 2406 total number of atoms and calculate the 'integral' heat of adsorption of atoms and molecules by a statistical average of the heat of adsorption at different sites. The bond order conservation model is then used to calculate the activation barrier for CO₂ formation as a function of the particle size. An analysis of the activation barriers for different steps indicates that for both the metals CO₂ formation is the rate limiting step. The calculated rate of CO₂ formation for both metal particles shows higher activity for smaller particles in total agreement with the experimental observations.

Studies on CO oxidation reaction are of enormous importance in the area of environmental catalysis. With the strict restrictions being imposed on emission from automobiles, particularly in the industrialised nations, it is becoming essential to minimise CO emission along with NO and other hydrocarbons. The reaction has, therefore, been extensively studied on supported metals as well as on single crystals. Since the metals suitable for catalysing the CO oxidation are generally precious metals it is important to minimise their use by preparing very well-defined small metal particles. In this work we have studied the size dependence of the CO oxidation reaction on Pd and Rh metal particles. Several experiments done on these systems show that the CO oxidation reaction is generally structure insensitive; and in some cases the rate of CO₂ formation is higher for smaller particles. A model, based on the bond-order conservation-Morse-potential (BOCMP), is used in this work to show that for practical catalyst particles with the number of atoms in the range of 200-2400 the CO oxidation rate marginally increases with decreasing particle size.

The Theoretical Model

In order to understand the energetics and mechanism of catalytic reactions it is important to know accurately the heat of adsorption of atoms and molecules on the catalyst surface. Because of particle morphology there are several adsorption sites on a particle. For example, for the fcc cubo-octahedral particles there are the corner sites, the edge sites, the fcc(111)-like face sites and fcc(100)-like face sites. It is difficult to know either experimentally or theoretically the heat of adsorption of an adsorbate at these sites separately. Experimentally, it is only the microcalorimetry that can give an estimate of the particle-average heat of adsorption, also known as the integral heat of adsorption. In theory, on the other hand, one can calculate the heat of adsorption only at some symmetric sites of the single crystal surfaces. To understand the energetics of surface reaction on particles it is important, therefore, to have some model for calculating the heat of adsorption. In this context, the bond-order conservation-Morse-potential model of Shustorovich is very useful. This model is an empirical model by which it is possible to estimate the heat of adsorption at any type of site from the knowledge of the heat of adsorption at some other type of sites. For example, if $Q_{ad}^{0}$ be the heat of adsorption of an atom on the top site, then for a site with $n$ nearest neighbours, the heat of adsorption would be

$$Q_{ad} = Q_{ad}^{0} (2 - 1/n)$$

(1)
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Table 1 - Structural characteristics of a few cubo-octahedral particles

<table>
<thead>
<tr>
<th></th>
<th>$N^T$</th>
<th>$N^S$</th>
<th>$N^{C_3}$</th>
<th>$N^{C_4}$</th>
<th>$N^{C_7}$</th>
<th>$N^{C_8}$</th>
<th>$N^{C_9}$</th>
<th>$n$</th>
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<tr>
<td></td>
<td>38</td>
<td>201</td>
<td>586</td>
<td>1289</td>
<td>2406</td>
<td>32</td>
<td>201</td>
<td>586</td>
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<tr>
<td></td>
<td>32</td>
<td>122</td>
<td>272</td>
<td>482</td>
<td>752</td>
<td>32</td>
<td>122</td>
<td>272</td>
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<tr>
<td></td>
<td>24</td>
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<td>24</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>36</td>
<td>72</td>
<td>108</td>
<td>144</td>
<td>0</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>6</td>
<td>24</td>
<td>54</td>
<td>96</td>
<td>0</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>56</td>
<td>152</td>
<td>296</td>
<td>488</td>
<td>8</td>
<td>56</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>7.58</td>
<td>9.43</td>
<td>10.20</td>
<td>10.61</td>
<td>10.87</td>
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</tr>
<tr>
<td></td>
<td>6.75</td>
<td>7.77</td>
<td>8.11</td>
<td>8.29</td>
<td>8.39</td>
<td>6.75</td>
<td>7.77</td>
<td>8.11</td>
</tr>
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</table>

The above empirical relation has been found to be qualitatively correct from a comparison of the experimental heat of adsorption values at different sites. For a nanoparticle with cubo-octahedral geometry we can have adsorption sites with $n$ in the range 1-4. In Table 1 we have shown the structural characteristics of a few particles with cubo-octahedral geometry. For a particle with total number of atoms, $N_T$, this table shows the total number of surface atoms, $N_s$, and the number of atoms with different surface coordination numbers $N_C$ ($j = 6$ - 9), the average coordination $(n)$ per atom in the particle and the average coordination $(n_s)$ of an atom in the surface such that $\Sigma N_C = N_T$.

It may reasonably be assumed that the corner atoms offer adsorption sites with number of nearest neighbour $n = 1$; while the edge atoms offer adsorption sites with $n = 2$. Also, the fcc(111)-like and fcc(100)-like faces offer adsorption sites with $n = 3$ and $n = 4$ respectively. Then the data in Table 1 and the relation (1) may be used to find the average adsorption energy of a particle as

$$Q_{av} = \left(\frac{1}{N_s}\right)\sum_n P_n U_n$$

where $P_n$ is the number of adsorption sites with $n$ nearest neighbours. This energy may be considered as equivalent to the experimentally measured integral heat of adsorption. In Figure 1 (a) and (b) we plot the variation of this particle-average adsorption energy of O, CO and CO$_2$ on Pd and Rh respectively. For both the metals, it may be noticed that, the variation is small for $N_T > 500$.

**Results and Discussion**

In the overall CO oxidation process there are several steps like (a) CO adsorption, (b) O$_2$ adsorption and dissociation, and (c) recombination of adsorbed CO (CO) with adsorbed O (O) to form CO$_2$ (ref.18). In studying the kinetics of the CO oxidation it could be of interest to know the sticking coefficient of CO and O to the metal surfaces, and then calculate the equilibrium concentration of CO and O on the surfaces. These information could be used to calculate the rate of CO$_2$ formation. However, in this work we would be mainly interested in the energetics of the reaction and hence we would compare the relative magnitude of the heat of adsorption of CO and O, the activation energy for dissociation of O$_2$ and the activation energy for recombination of CO$_2$ with O$_n$ to form CO$_2$. It is well known that CO is molecularly adsorbed on both Rh and Pd. However, O$_2$ is spontaneously dissociatively adsorbed on both these metals in the single crystal phase as well as on the aggregate phase as may be found from the following BOCMP values of activation barriers for dissociation ($E^*$) of O$_2$:

<table>
<thead>
<tr>
<th></th>
<th>$Q_{av} (\text{O}_2)$</th>
<th>$E^* (\text{O}_2 \text{dissociation})$(kcal/mol)</th>
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<tr>
<td>Pd</td>
<td>13.4</td>
<td>$N_T = 38$</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>$N_T = 2406$</td>
</tr>
<tr>
<td>Rh</td>
<td>15</td>
<td>-1.5</td>
</tr>
<tr>
<td></td>
<td>-22.5</td>
<td>$N_T = 2406$</td>
</tr>
</tbody>
</table>

Fig. 1 - Heat of adsorption of O, CO and CO$_2$ on (a) Pd and (b) Rh particles. $N_T$ is the number of atoms per particle.
It may be noticed from the above values that the activation barrier for dissociation of $O_2$ is much lower than the activation for its desorption. Thus we have molecularly adsorbed CO and adsorbed oxygen atom to form the $CO_2$. The activation for this recombination reaction, is given by the simple BOCMP model relation

$$E'(CO_2) = \left[ Q_0 \cdot Q_{co}/(Q_0 + Q_{co}) \right]$$

... (3)

The resulting activation energies for recombination of CO and $O$ on the Pd and Rh metal particles are shown in Fig. 2. It may be noticed that for all particles sizes the activation barrier for recombination is higher than both the CO desorption energy and the activation energy for $O_2$ dissociation. This suggests that $CO_2$ formation is the rate-limiting step in the overall $CO$ oxidation reaction on both the metals. From the Figs 1 and 2 it may be noticed that for particles with the number of atoms more that 500 the adsorption energy or the activation energy increases slightly with particle size. The activity of the metal particles can then be roughly estimated as

$$r = A \exp(-E'/RT)$$

... (4)

where $A$ is an arbitrary constant that depends on the collision frequency of the gas molecules on the surface and the geometrical factor of the adsorption complex. In the absence of accurate knowledge about these parameters $A$ cannot be explicitly known for all the particle sizes. We, therefore, consider $A$ as a constant and plot the exponential function which mainly controls the $CO_2$ formation rate. The dependence of $r$ on particle size is shown in Figure 3 for a typical temperature of 450 K. It may be noticed that for both the metals the activity for $CO_2$ formation increases moderately as the particle size decreases from 2400-atom to 200-atom size. However, for still smaller particle size the activity increases faster by a few orders of magnitude. But particles with atoms less than approximately 200 atoms may not show the metallic property. And, therefore, for all practical purposes, the particles in the size range of $200 < N_T < 5000$ are supposed to be of real importance in catalysis. In this range Pd may be marginally better $CO$ oxidation catalyst than Rh.

At this stage it is worthwhile to compare the above predictions with the experimental results. So far as the Rh particles are concerned, Oh and Eickel's studied the kinetics of $CO-O_2$ reaction on supported Rh particles to find that the specific rate increases moderately with decreasing particle size. Very technique. Their experimental results showed that smaller particles were more active in $CO_2$ production.

Again, for Pd particles there are several experiments which show more or less similar dependence of $CO_2$ formation rate on the particle size. For example, Ladas et al. studied $CO$ oxidation on recently, Nehasil et al. also studied $CO$ oxidation on alumina-supported Rh particles by the transient experiment of molecular beam surface scattering model Pd/Al$_2$O$_3$ catalyst and found that the specific rate of $CO_2$ formation mildly increases with decreasing Pd particle size. Similar conclusions were drawn from the recent experiments of Rainer et al. on Pd particles. Thus, the present results based on BOCMP model are in total qualitative agreement with the experimental results.

In this work we did not look for quantitative agreement with the experimental results, because this is a model study where the activity is calculated
from the activation barrier for a single step in the overall oxidation reaction. In the experiment, on the other hand, every step influences the overall activity; and the activation barrier, also known as the apparent activation barrier, has the contribution from all possible steps.

In this work, it is assumed that at temperatures in the range of 700 -800 K and at higher coverages adsorption will be a dynamic process and adsorption will take place on various sites of the particles. It is important therefore to identify the average adsorption energy as experimental integral heat of adsorption. BOCMP model, in spite of its certain drawbacks, helps one to find easily this average adsorption energy.

Furthermore, in this work it is more or less the geometrical effects that are considered in studying the CO oxidation rate. The electronic effects are not explicitly studied in this work since for particles with more than 200 atoms the band width and density of states would not drastically change with increase in particle size.

**Conclusions**

Within the limitations of the bond order conservation Morse potential (BOCMP) model, the energetics of the different steps in the CO oxidation reaction on metal particles have been studied. We have found the adsorbate binding energy, activation barrier for O₂ dissociation and the activation energy for recombination of CO and O as a function of the particle size. From an analysis of the energetics, the rate-limiting step has been identified and the activity of the particles has been calculated which shows qualitative agreement with the available experimental results.

**Acknowledgement**

One of the authors (M.M) thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, for the award of a Senior Research Fellowship to carry out this work.

**References**