Physical properties of supported and unsupported transition metal nanoclusters

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Introduction

Supported nanoclusters play a major role in many physical and chemical processes, such as those in heterogeneous catalysis and in the fabrication of nanostructured materials tailored to specific technological applications, e.g., micro and nanoelectronics, optoelectronics, and magnetic devices. Physical and electronic properties of metal nanoclusters deposited on various substrates have recently received a great deal of attention. In particular, carbon-supported platinum particles are commonly used as catalytic materials in gas and liquid reactions. Due to the high cost of platinum, many efforts are directed to optimizing its catalytic performance, which in turn requires a substantial understanding of the catalyst/substrate interactions, and of the relationships between size, shape, and activity of the nanocatalysts. To minimize costs, alternative bi- and trinmetallic catalysts are proposed for several catalytic processes. In these cases, the mixing of the different elements on the surface of the nanoparticle gives rise to unexpected electronic and physical effects.

Computational methods

We use molecular dynamics (MD) simulations to compute the time evolution of a system consisting of a metal cluster of nanodimensions either in vacuum or deposited on a graphite substrate. The metal-metal interactions are treated within the Sutton-Chen potential model, whereas the metal-graphite interactions are described by a Lennard-Jones potential. Details of the computational methods are given in a previous study. Heating and cooling curves are determined for each nanocluster and the melting temperature is obtained by the transition observed in the potential energy curve versus temperature. The melting/freezing characteristics are obtained for different cluster sizes and shapes.

Bimetallic systems are studied using a combination of Monte Carlo (MC) and MD methods. The MC technique is used to obtain the equilibrium atomic distribution on a bimetallic cluster of a given shape and size. This equilibrium distribution is used as input to MD simulations where the dynamics of the system is investigated.

Results and Discussion

Figure 1 shows the variation of the potential energy for the 256-atom cube-shaped Pt cluster. In the heating process (squares), there is a clear energy jump in the temperature range from 1000 to 1100 K, this is due to the melting transition, note that the cluster melting temperature is much lower than that of bulk Pt metal (2041.15 K as determined experimentally). The second set of data in Figure 1a corresponds to the cooling curve (circles), where the temperature is lowered starting from 1800 K down to 300 K. The system also shows a sharp liquid-solid transition, the freezing temperature, at T between 1000 and 900 K. The same time step was used for heating and cooling processes. Note that the portion of the curves corresponding to T > 1000 K are coincident for the cooling and heating processes, whereas for the portion below the melting temperature the potential energy is higher for the heating than for the cooling process. This indicates that the annealing process can easily find the lowest energy state for a given temperature, whereas during the heating process the system gets trapped in metastable states. Eventually, for simulation times sufficiently long, both curves should also agree at T < T_{melting}.

Similar phenomena have been observed in simulations of unsupported gold nanoclusters. Another interesting behavior is observed also in the heating curve (Figure 2a), where the potential energy decreases from its value at 600 K to a lower value at 700 K and then increases again when T reaches 800 K. At 600 K, the cluster changes shape due to surface melting and surface atomic diffusion, adopting a semi-spherical shape. This change has also been observed in the experiment using high-resolution transmission electron microscopy, and it is attributed to a structural solid-solid transition.

The melting behavior depends on the shape and size of the cluster. A spherical cluster constructed by carving the surface of a fcc cluster and deposited on the static surface of graphite is also studied. The potential energy for the 260-atom ball-shaped cluster is displayed in Figure 1b for the heating and cooling processes. Upon heating, the ball cluster also undergoes a solid-liquid jump in the temperature range from 1000 to 1100 K (squares), although the slope of the heating curve changes again at 1200 K. Practically no hysteresis is found between the heating and cooling curves at the liquid-solid transition for the ball-shaped cluster, as opposed to the case of the cubic cluster. This suggests that hysteresis loops may be more likely to be found in local minimum structures. The ball-shaped cluster also exhibits a behavior similar as that calculated for the cubic cluster at a temperature right below the melting transition, at T between 800 and 900 K, where the potential energy changes to a lower energy state presumably due to a solid-solid transition. We suggest that the clusters undergo surface melting and surface atomic diffusion to form a lower energy structure before melting, as discussed in more detail below. Upon cooling, as in the case of the cubic cluster, the potential energy (circles) in the liquid range approaches values close to those of the heating process, whereas it reaches lower values in the solid region.

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**Table 1:**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>E_p (Kev)</th>
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<tr>
<td>200</td>
<td>-1.42</td>
</tr>
<tr>
<td>400</td>
<td>-1.38</td>
</tr>
<tr>
<td>600</td>
<td>-1.34</td>
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<td>800</td>
<td>-1.30</td>
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<tr>
<td>1000</td>
<td>-1.26</td>
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</tbody>
</table>

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**Figure 1:**

(a) Cube Cluster

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Figure 1. Calculated potential energy ($E_p$) variation, in KeV, for the heating (squares) and cooling (circles) curves. (a) Cube-shaped cluster. (b) Ball-shaped cluster.

Conclusions

The melting transition for a 256-atom Pt cluster of cubic shape deposited on a static graphite substrate is found in the range between 1000 and 1100 K, and the freezing temperature between 900 and 1000 K. At 600 K the cubic cluster starts experiencing a structural transformation, which is evidenced at 700 K by an increase in the interlayer separations from 1.83 to 2.13 Å, the outermost surface layers melt, and their atoms migrate to the layers closer to the substrate, a temperature-induced wetting phenomenon. At temperatures higher than 1000 K, melting takes place.

Results on bimetallic systems will be presented at the meeting.

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References
