Catalysis Letters 15 (1992) 57–64

An investigation of the shape of small platinum clusters using the embedded atom method

A. Sachdev [1], R.I. Masel [1]* and J.B. Adams [2]

[1] *Department of Chemical Engineering, 1209 W. California and* [2] *Department of Materials Science and Engineering, 105 S. Goodwin, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*

The equilibrium shape and structure of small platinum clusters with 5–60 atoms was investigated using the embedded atom method (EAM). An analysis of the stability of the clusters with polyhedral symmetries indicated that, except at the magic number sizes, the clusters spontaneously reconstructed to more stable shapes at 0 K. Even the magic number icosahedra and cubo-octahedra were unstable upon annealing at 500 K. The clusters which reconstruct to lower energy structures appear to be highly asymmetric and irregular. Many different structures were found to have similar energies. The annealed clusters also display surface features not found in bulk platinum.

Keywords: Platinum particles; active sites; embedded atom method; catalyst microstructure

1. Introduction

The shape and structure of small metal particles is quite important in the understanding of supported metal catalysts. Even though substantial advances in the theoretical and experimental techniques for studying small clusters have been made in recent years [1,2], the results from a classic and thorough analysis of small argon clusters performed by Hoare et al. [3–5] have served as the models for the structure of ideal small metal particles in supported metal catalysts. A primary outcome from this previous investigation was that the icosahedron and the cubo-octahedron were the most stable symmetries available to small clusters or particles. Yet, in experimental observations of supported metal catalysts most of the symmetries of the small metal particles tend not to

* To whom correspondence should be addressed.

be these ideal polyhedral types but instead display structural features such as twinning, stacking faults and other defects [6–8]. These findings are particularly true in studies of small fcc metal particles formed by vacuum evaporation.

In this study a modern calculational procedure called the embedded atom method (EAM) was used to examine the equilibrium shape and structure of small platinum clusters. In a previous investigation Bigot and Minot [9] used extended Hückel theory to determine the shapes of platinum clusters up to 13 atoms in size. In the work described here, we have extended these calculations to larger clusters. We chose to use the embedded atom method rather than the extended Hückel method because previous workers have found that the EAM gives better agreement with experimental values. The EAM method has been used to reproduce the experimental shapes of 3–6 atom Pt clusters adsorbed on field emitter tips [10,11]. It has also been found to reproduce the surface reconstructions in bulk platinum systems [12]. Therefore, the EAM seemed useful for our studies.

In the work reported here we calculated the energies and stabilities of clusters ranging in size from $N = 5$–60 atoms with various polyhedral symmetries. In addition a series of simulated annealing runs were undertaken to search for lower energy structures at each cluster size.

2. Methods

All the calculations in this paper were done using techniques described elsewhere [13]. We started with a 5–60 atom cluster with an icosahedral, cubo-octahedral, tetrahedral or octahedral symmetry and calculated its energy. Conjugate gradient minimization [14] was then used to relax the cluster to its local minimum energy configuration. A search for lower energy structures was performed using simulated annealing. The result was a plot of the structure and energy of clusters as a function of cluster size.

All of the calculations used the embedded atom method (EAM) to calculate cluster energies. Detailed explanations of this technique can be found elsewhere in the literature [15,16]. In the EAM procedure the contribution to the total energy of an atomic system is determined from two components, namely the embedding energy and the electrostatic pair repulsion term. The embedding energy is defined as the energy required to introduce an atom into the local electron density created by the presence of the neighboring atoms. The electrostatic pair repulsion term is essentially the two body repulsion term between adjacent atomic cores. The EAM has proved to be successful in evaluating the energetics and structures of various surfaces of transition metal elements including platinum [12]. We used standard EAM functions from the literature; one is referred to Sachdev et al. [13] for further details.

3. Results and discussion

3.1. CLUSTER STABILITY

In order to test the relative stability of the various cluster symmetries and sizes we carried out conjugate gradient minimizations on them and evaluated the changes in the cluster structure. We began with a polyhedral cluster, such as an icosahedron, with bulk lattice parameters and relaxed it to its local minimum configuration. The results of these calculations showed that the clusters retained their basic shape only at their magic number sizes. The 13 and 55 atom icosahedral and cubo-octahedral clusters contracted when they were relaxed, but did not change their symmetry. The 45 atom octahedron and the 57 atom tetrahedron clusters underwent only a slight distortion. However, all of the other icosahedral, cubo-octahedral, octahedral and tetrahedral clusters were found to be unstable and readily relaxed into structures which did not resemble the initial polyhedral symmetry. For example, fig. 1 shows an example of a 14 atom truncated icosahedron which spontaneously reconstructed into a structure with a highly irregular symmetry. The 14th atom, which was initially located on the second shell of the icosahedron was found compressed into the first layer after the reconstruction.

Even though the non-magic number clusters were unstable we were still interested in obtaining their energy values as a means of making quantitative comparisons between differing cluster symmetries and sizes. This was accomplished by devising a cluster growth sequence. In this algorithm a polyhedral cluster was grown from its first shell structure by adding additional atoms sequentially at the most favorable available second shell position. The sequence was terminated when the second shell coordinates were completely occupied. For instance, the icosahedral growth sequence was initiated from the first shell cluster core, consisting of $N = 13$ atoms; the subsequent sites were filled from

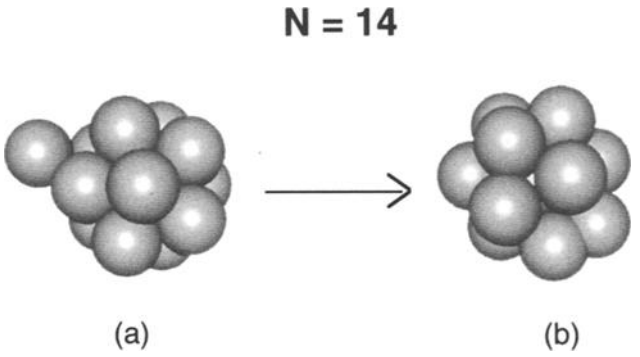

Fig. 1. An example of the reconstruction which takes place after relaxing a non-magic number truncated icosahedron. (a) Initial 14 atom truncated icosahedron, $E = -60.78$ eV, (b) minimized 14 atom cluster, $E = -62.87$ eV.

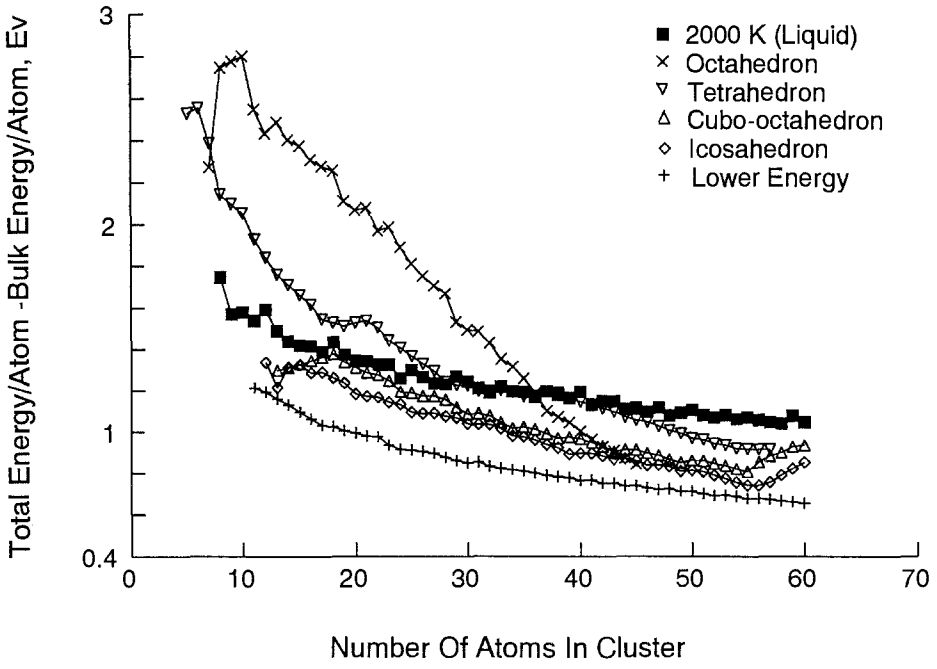

Fig. 2. The average energy of various polyhedral clusters as a function of cluster size. The energies of the lower energy structures are also plotted.

the remaining positions of a separately relaxed $N = 55$ or two shell icosahedron. The criterion at each step was the lowest possible energy for the overall cluster. It should be emphasized that all the intermediate size or truncated polyhedral clusters were not completely stable; they would certainly reconstruct into vastly different structures when re-relaxed.

Fig. 2 shows the growth sequence plots for the different polyhedral symmetries considered. In addition average energy values of liquid clusters obtained at 2000 K by Monte Carlo simulation were acquired for all cluster sizes. The icosahedral and the cubo-octahedral clusters were the most energetically competitive of the polyhedral clusters. The additional stability at the magic numbers is evidenced by a slight dip in the growth sequence plot. The tetrahedra and the octahedra can be seen to be especially unstable at the smaller sizes, however, at the intermediate sizes of growth sequences all clusters appear to have very similar energy values.

3.2. LOWER ENERGY STRUCTURES

A simulated annealing procedure was followed to examine the structure of any clusters which may happen to have total energy values lower than the previously determined low energy structure, i.e. the magic number icosahedra.

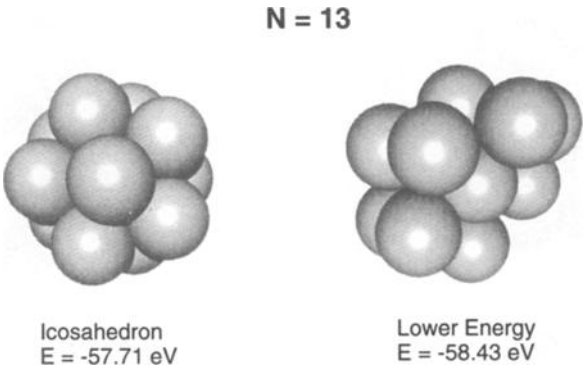

Fig. 3. A 13 atom icosahedron and the lower energy cluster obtained after simulated annealing.

As mentioned earlier, the cluster was annealed at 500 K for 2000 Monte Carlo steps followed by quenching to 0 K using the conjugate gradient minimization. This sequence was iterated for a total of 2 million MC jumps. There is no guarantee that the lowest energy structure found is the global minimum for the system, however precautions were taken to make sure that our lower energy structure was independent of the starting configuration as well as the number of iteration steps.

Examples of these lower energy structures of sizes 13, 20, 40, 55, and 60 are illustrated in figs. 3 and 4. As can be observed, these new clusters are highly asymmetric, irregular and defected compared to the polyhedral clusters. They also happen to be more compact than their non-magic number polyhedral cluster counterparts which could partially account for their enhanced stability. It is not feasible to obtain what could be construed as a nearest neighbor distance from the central atom in these clusters. Instead a radial distribution histogram provides us with some way of quantifying the cluster structure by plotting the frequency of the interatomic distances within an individual cluster. Fig. 5 displays these distributions for a representative polyhedral cluster as well as for the corresponding lower energy structure. The histograms for the lower energy structures show a more gradual distribution in the interatomic distances than a icosahedron which indicates distribution with more discrete peaks. Although these histograms indicate traits characteristic of liquids, we find that the cluster shapes are relatively stable. In dynamical calculations we do not observe the rapid changes in shape characteristic of liquids. As a result, we suggest that the dynamical behavior of these clusters is more solid-like than liquid-like. A detailed investigation of the dynamical properties is currently in progress.

Another result of interest is the existence of clusters at the smallest sizes which have very comparable energies but very dissimilar shapes and structures. In the $N = 13$ atom system an entire series of clusters is within 0.4 eV of the lowest energy cluster found. This trend of the presence of many different cluster

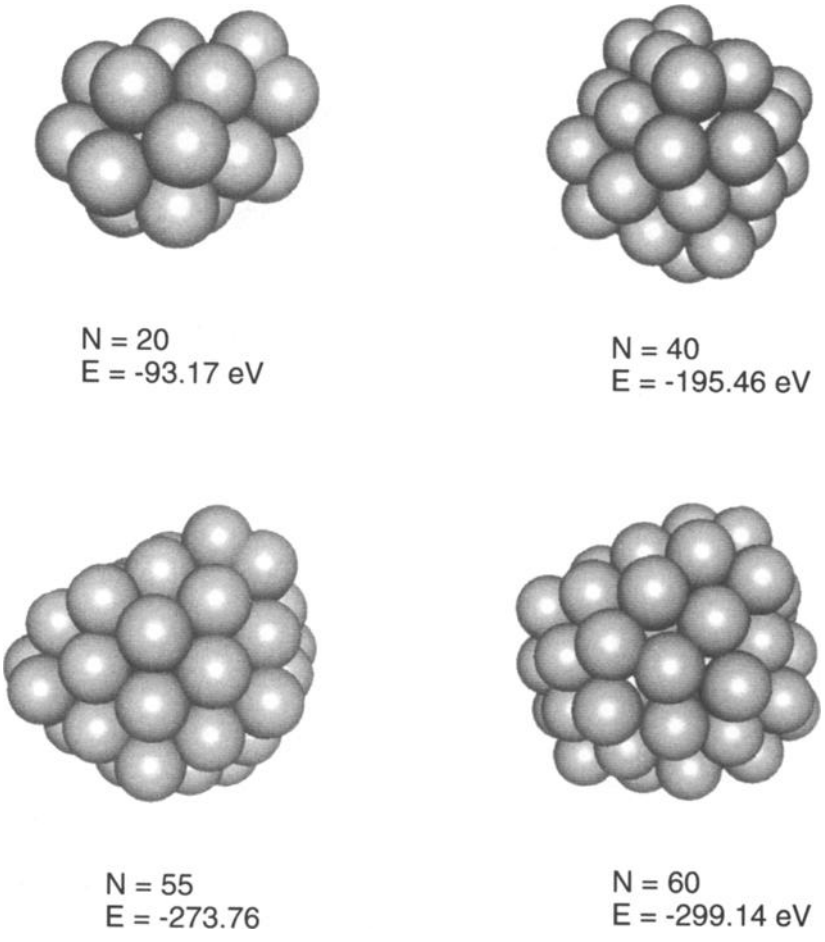

Fig. 4. Lower energy structures for a few representative cluster sizes.

shapes with similar energies or isomeric structures was also observed in the extended Hückel calculations of small platinum clusters [9].

This result has an important implication in catalysis. If we have several different structures with very similar energies then small changes due to the presence of a support or an adsorbate can cause one structure to be favored over the other. In our previous publications [17,18] we have shown that particles can reconstruct in the presence of adsorbates. Our EAM calculations are fully consistent with our previous experimental findings. For example fig. 6 shows how hydrogen changes the shape of a Pd cluster. The icosahedral symmetry was found to be the most stable for a clean $N = 13$ palladium cluster. However, after including the interactions of approximately one monolayer of hydrogen, the icosahedral palladium cluster was found to undergo a change to a more cube-like shape.

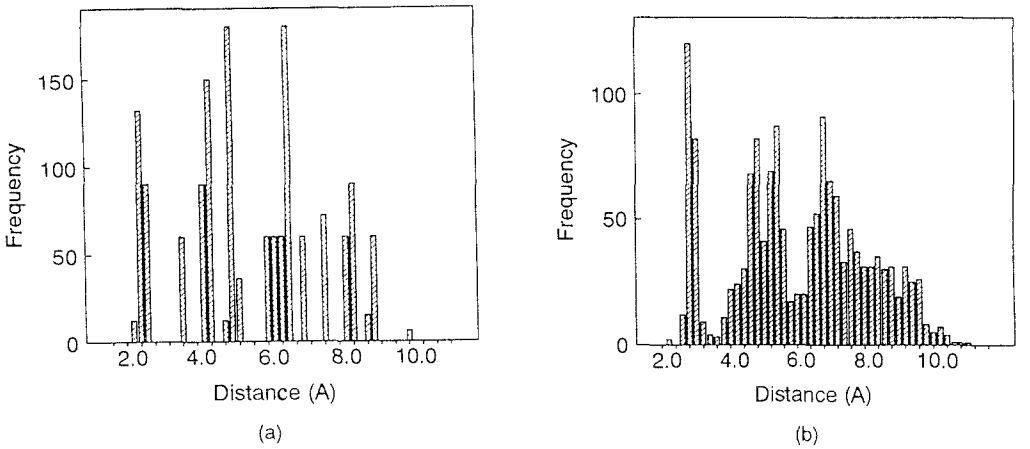

Fig. 5. Radial distribution histograms indicating the distribution of interatomic distances within a cluster (a) $N = 55$ icosahedron, (b) $N = 55$ lower energy structure.

4. Conclusions

We have been able to find the structure of a series of platinum clusters consisting of up to 60 atoms which are more stable than the icosahedral or the cubo-octahedral symmetries. These lower energy structures which appear to be highly defected and asymmetric are also very variable. Structural defects are also characteristic of the small metal particles commonly observed in TEM images of supported metal catalysts. At present our calculations do not take into account the effect of the support on the structure of the platinum clusters. It is conceivable that such an interaction could lead to vastly different cluster symmetries. Yet, this EAM investigation does demonstrate that some of the old

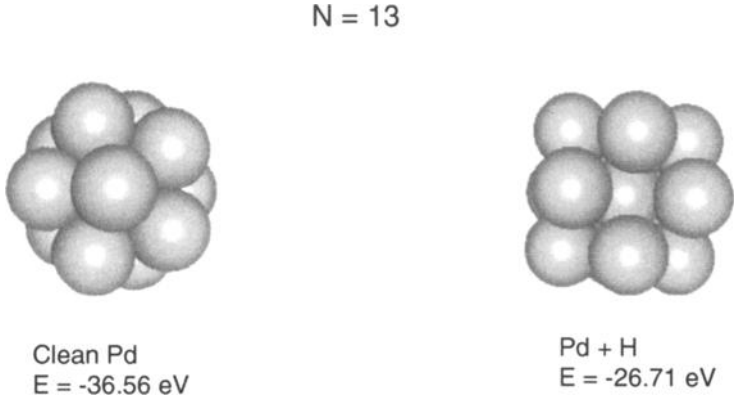

Fig. 6. The effect of adsorbed hydrogen on the equilibrium shape of a palladium cluster. (left) A clean $N = 13$ Pd cluster indicating the icosahedral symmetry, (right) a $N = 13$ Pd cluster after accounting for the interactions with 42 adsorbed hydrogen atoms on its surface. A cube-like morphology is indicated.

ideas regarding the stable shapes of small metal clusters do not apply to platinum.

Acknowledgement

This work was supported by the National Science Foundation under Grant DMR 89-20358. The authors would also like to thank Dr. M.S. Daw, Dr. S.M. Foiles and Dr. M.I. Baskes for providing them with the EAM codes.

References

[1] R.L. Whetten, D.M. Cox, D.J. Trevor and A. Kaldor, Surf. Sci. 156 (1985) 8, and references therein.
[2] J. Koutecky and P. Fantucci, Z. Phys. D 3 (1986) 147.
[3] M.R. Hoare and P. Pal, Adv. Chem. Phys. 20 (1971) 161.
[4] M.R. Hoare and P. Pal, Adv. Chem. Phys. 24 (1975) 645.
[5] M.R. Hoare and J. McInnes, Adv. Phys. 32 (1983) 791.
[6] M.J. Yacaman, K. Heinemann, C.Y. Yang and H. Poppa, J. Cryst. Growth 47 (1979) 187.
[7] L.D. Marks and D.J. Smith, J. Cryst. Growth 54 (1981) 425.
[8] A. Howie and L.D. Marks, Phil. Mag. A49 (1984) 95.
[9] B. Bigot and C. Minot, J. Am. Chem. Soc. 106 (1984) 6601.
[10] P.R. Schwoebel, S.M. Foiles, C.L. Bisson and G.L. Kellogg, Phys. Rev. B40 (1989) 10639.
[11] A.F. Wright, M.S. Daw and C.Y. Fong, Phys. Rev. B42 (1990) 9409.
[12] S.M. Foiles, Surf. Sci. 191 (1987) L779.
[13] A. Sachdev, R.I. Masel and J.B. Adams, J. Catal., to be published.
[14] J.E. Sinclair and R. Fletcher, J. Phys. C7 (1974) 864.
[15] M.S. Daw and M.I. Baskes, Phys. Rev. B29 (1984) 6443.
[16] S.M. Foiles, M.I. Baskes and M.S. Daw, Phys. Rev. B33 (1986) 7983.
[17] W.H. Lee, K.R. van Loon, V. Petrova, J.B. Woodhouse, C.M. Loxton and R.I. Masel, J. Catal. 126 (1990) 658.
[18] W.H. Lee, V. Petrova, K.R. van Loon, J.B. Woodhouse, C.M. Loxton and R.I. Masel, Proc. Mat. Res. Soc. Symp. 194 (1990) 221.