PAK Publishing Group
Growing Knowledge for Future

Proceedings Book of ICETSR, 2014, Malaysia
Handbook on the Emerging Trends in Scientific Research
ISBN: 978-969-9347-16-0

Scrutiny of Shape-Dependent Catalytic of Au-Pt, Au-Pd, and Pt-Pd Nanoparticles from Temperature View Point

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Abstract

Nano catalysis is a very active field, so there are a few studies in the shape dependent catalytic properties of transition metals from a thermodynamics approach. Transition metal nanoparticles are very attractive due to their high surface to volume ratio. In this paper, we study about the Aurum (Au) - Platinum (Pt), Au-Palladium (Pd) and Pt-Pd catalyst. The Face-Centered-Cubic (FCC) structure of Pt, Pd, and Au has been considered in this model. The shape stability of them has been discussed and Size-dependent melting temperature of Au is studied for the first time. The most and the least variation of transition temperature is related to tetrahedron and dodecahedron geometry for all three groups of catalysts.
Keywords: Nano, Catalyst, Shape, Melting, Metal.

1. Introduction

Much of the energy produced in the world is wasted. Finding ways to save energy in these processes play an important role in reducing energy consumption. Using nano technology in catalysts can produce more efficient and can save energy. Nano catalyst is the catalysts at the nano scale (one billionth of a meter). In the other word, it is the combination of the developed area of the catalyst and nanotechnology. If nano catalyst added to a reaction mixture, the reaction rate increases, without having to participate in the chemical reactions. A classic example of catalysts is platinum which is used in car exhaust systems. Although the old catalysts are still effective but with advancement in nano science, efficient catalysts in the oil and gas industry has been created. If the catalyst is larger, they are also more efficient because more molecules react at the same time. Maximizing the surface area of the catalyst nanoparticles is not the only reason as a heterogeneous catalyst. Indeed, size of the fine crystals in metal catalyst has a great effect on the catalytic activity. Using bimetallic nanoparticles catalyst, metal catalyst improves. Bimetallic nanoparticles exhibit unusual properties different from their bulk behavior. These properties are determined by their size, shape and composition. Bimetallic catalyst consists of two different metallic elements. When considering metallic catalysts, platinum is a

standard material but this material is most expensive than gold. Therefore, to reduce the amount of platinum and then the cost of the application one possible way is to use an alloy of platinum with another metal. In year of 2011 Guisbires and et al proposed a model for size dependent catalytic and melting properties of platinum-palladium nanoparticles. Thermodynamics may provide useful insights in nanotechnology. With this approach, the size and shape effects on melting temperature and enthalpy are investigated.(Deng *et al*.,2010),(Maye *et al*.,2004)Thermodynamics point of view, the overall free energy, ($G_{nanoparticle}$), gathering energy mass, (G_{balk}) and the surface energy($G_{surface}$). Surface tension and free energy components of the phase stability of nanoparticles are important.

Face centered cubic (FCC) metals Pt, Pb and Au may exhibit a variety of geometrical shapes. These shapes are: dodecahedron, icosahedron, cub octahedron, cube, octahedron and tetrahedron.

In this paper, first we are using classical thermodynamics to study the size and shape effects on melting temperature of nanostructure materials then we study on the size effect of the geometrical shapes of platinum, palladium and gold nanoparticles on the melting temperature and we calculate the stabilities of these shapes according to the area/volume. Also, we study on the thermodynamics variations of a solid in nano scale.

2. The Effects of Nano Catalyst Structure on the Melting Temperature Using Thermodynamics Approach

Gibbs free energy of a nanostructure can be expressed as a sum of the bulk free energy G_{∞} with the expression that is considered the effects of the surface nanomaterial (Barnard and Zapol, 2004), (Montejano-Carrizales *et al*., 2006), (Wang *et al*.,1998)

$$G = G_{\infty} + (\frac{A}{V})\gamma \quad (1)$$

A and V are the surface area and volume of the nanostructure, respectively and γ is the surface energy. At a fixed temperature T, Gibbs free energy difference between the liquid and solid phases for a nanostructure is given by

$$G_l - G_s = G_{l,\infty} - G_{s,\infty} + \left(\frac{A}{V}\right)(\gamma_l - \gamma_s) \quad (2)$$

The phase transition occurs when Gibbs free energy difference equals zero. At, T=$T_{m,\infty}$;

$$G_{l,\infty} - G_{s,\infty} = \Delta H_{m,\infty} - T_{m,\infty}\Delta S_{m,\infty} = 0 \quad (3)$$

At T=T_m

$$G_l - G_s = \Delta H_m - T_m \Delta S_m = 0 \quad (4)$$

ΔH_m and $\Delta H_{m,\infty}$ are the size dependent melting enthalpy and bulk melting enthalpy, respectively and also ΔS_m and $\Delta S_{m,\infty}$ are the size dependent melting entropy and bulk melting entropy. At $T = T_m$ Eq. 2. becomes:

$$\Delta H_{m,\infty} - T_m \Delta S_m + \left(\frac{A}{V}\right)(\gamma_l - \gamma_s) = 0 \quad (5)$$

Finally from the above equation we obtain that:

$$\frac{T_m}{T_{m,\infty}} = 1 + \left(\frac{A}{V}\right)\left[\frac{(\gamma_l - \gamma_s)}{\Delta H_{m,\infty}}\right] \quad (6)$$

or

$$\frac{T_m}{T_{m,\infty}} = 1 - \frac{\propto_{shape}}{a} \quad (7)$$

$\propto_{shape}$ is defined as, where $\propto_{shape}$ is the shape factor of nanocrystals.

$$\propto_{shape} = \frac{Aa(\gamma_l - \gamma_s)}{(V\Delta H_{m,\infty})} \quad (8)$$

a is the size of the crystal nanostructure. When $T = T_{m,\infty}$ than Eq. 5. is converted to:

$$\Delta H_m - T_{m,\infty}\Delta S_m + \left(\frac{A}{V}\right)(\gamma_l - \gamma_s) \quad (9)$$

By inserting eq 6 in to eq 9 we conclude that

$$\Delta H_m = \left(\frac{T_m}{T_{m,\infty}} - 1\right)\Delta H_{m,\infty,} + T_{m,\infty}\Delta S_m \quad (10)$$

We know that $T_m = \frac{\Delta H_m}{\Delta S_m}$ and $T_{m,\infty} = \frac{\Delta H_{m,\infty}}{\Delta S_{m,\infty}}$,then Eq. 10. under the following form:

$$\Delta H_m = \left(\frac{T_m}{T_{m,\infty}} - 1\right)\Delta H_{m,\infty,} + (\frac{T_{m,\infty}}{T_m})\Delta H_m$$

From Eq. 6., the $\frac{\Delta H_m}{\Delta H_{m,\infty}}$ is converted to:

$$\frac{\Delta H_m}{\Delta H_{m,\infty}} = \frac{T_m}{T_{m,\infty}} \qquad (11)$$

3. Discussion

The size dependent melting temperature of Pt, Pd and Au are plotted in figures (1a, 1b and 1c) by using eq 6. The shapes that have been considered are sphere, tetrahedron, cube, octahedron, dodecahedron and decahedron (Barnard, 2006), (Guisbiers and Buchaillot, 2009), (Yacaman *et al*.,2001). The material properties of Pt, Pd and Au are indicated in Table 1.

From the experimental result we know that at the nanoscale, the shape which exhibits the highest melting temperature is one that minimizes the most Gibbs free energy. From figs (1a, 1b, 1c) we observe tetrahedron and dodecahedron structure have minimum and maximum melting temperature value, respectively. In the other way our calculations show that the value of $\mathbf{A/V}$ for dodecahedron is more than the tetrahedron nanostructure. Therefore, we conclude that tetrahedron with the most $\mathbf{A/V}$ has the lowest T_m and dodecahedron with the lowest $\mathbf{A/V}$ ratio has the most melting temperature and is thermodynamically more stable (Montejano-Carrizales *et al*., 2006).

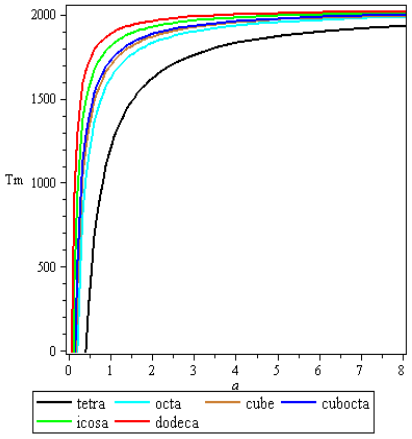
As we see in figure (1a, 1b, and 1c) the shapes that exhibit the maximum melting temperature are: dodecahedron, icosahedron, cub octahedron, cube, octahedron and tetrahedron respectively. Experimentally cub octahedron is observed for platinum nanoparticles. Whereas icosahedron, decahedron and cube octahedron are observed for palladium nanoparticles. We should care about compression results and experimental data. At the non-equilibrium conditions may be the thermodynamics theoretical is different from the experimental observation. In this condition the shape with the lowest A/V maybe is more stability. The size effect on the surface energies is low for higher sizes (Barnard and Zapol, 2004) Furthermore, edges and corners of the structures have an important role in the surface energy. We also can understand that the most variations of melting temperature are under the 20 nm for Au, Pd and Pt (Liang *et al*.,2002), (Lu and Jiang, 2004).

Table-1. Materials properties of platinum, palladium and gold.

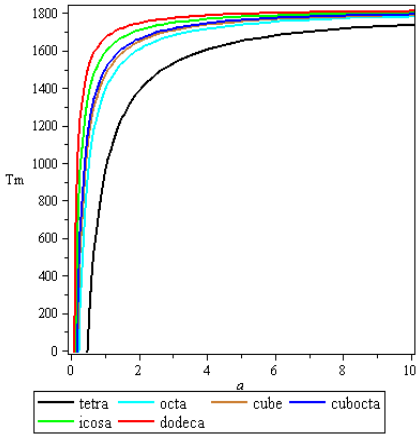
Material Properties	Pt	Pd	Au
$T_{m,\infty}(K)$	2041.5	1828	1327.3
$\Delta H_{m,\infty}(\frac{kj}{mol})$	22	17	12.5
$\Delta H_{sub,\infty}(\frac{kj}{mol})$	565	377	
$\gamma_l(\frac{j}{m^2})$	1866	1470	1120
$\gamma_s(\frac{j}{m^2})$	2.482	2.027	□□363

Fig-1.a. Size-dependent melting temperature of platinum versus the size for different shapes. b) Size-dependent melting temperature of palladium. c) Size-dependent melting temperature of Au (From Eq 6)

a)



b)



c)

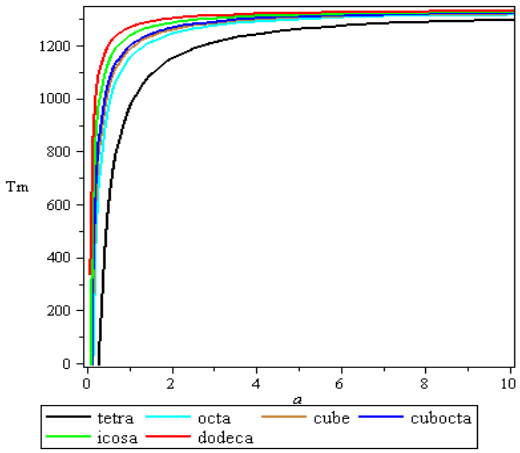
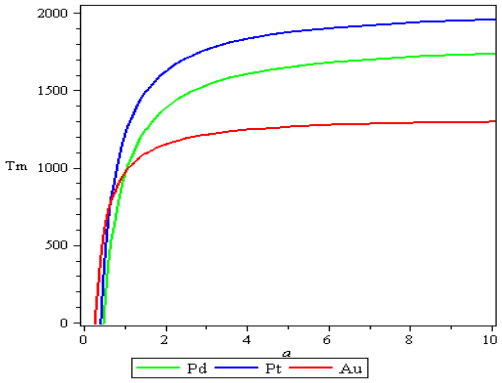
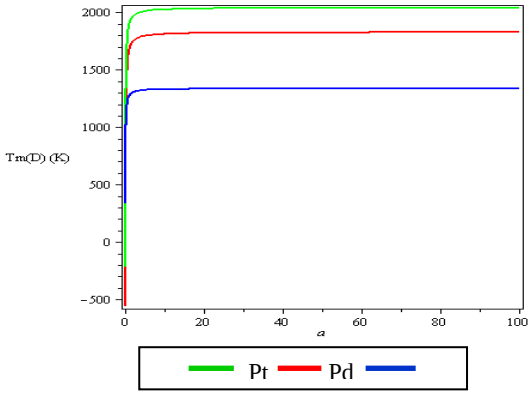


Fig-2. Compresion of melting temperature variation of Pd, Pt and Au.(a) for tetrahedron geometry.(b) for dodecahedron geometry (Eq 6)

(a)



(b)



As you see in the tables 2 and 3 the greatest variations in the melting temperature of the Pt, Pd and Au are related to tetrahedron geometry in the range of 0.5 to 1 nm. Also the least variations for dodecahedron structure are in the range of 5.5 to 6 nm. So in general we can say that Dodecahedron melting temperature in the range of 5.5 to 6 has the lowest variations and maximum change is in the tetrahedron at the range of 0.5 to 1nm. As before we mention about conclude that the Dodecahedron and tetrahedron geometry are the most and the last stable respectively.

Table-2. Melting temperature numerical values of the geometric shape cubes, Tetrahedron, octahedron for gold, platinum and palladium. (from Eq 6)

D	$T_m(D)(K)$								
	tetrahedron			octahedron			cube		
	Pt	Pd	Au	Pt	Pd	Au	Pt	Pd	Au
.5	361.2	54.8	590.4	1201.3	941.4	963.8	1355.5	1104.1	1032.3
1	1201.3	941.4	963.8	1621.4	1384.7	1150.5	1698.5	1466.0	1184.8
1.5	1481.4	1236.9	1088.3	1761.4	1532.4	1212.8	1812.8	1586.7	1235.6
2	1621.4	1384.7	1150.5	1831.4	1606.3	1243.9	1870.0	1647.0	1261.0
2.5	1705.4	1473.3	1187.9	1873.4	1650.6	1262.6	1904.3	1683.2	1276.3
3	1761.4	1532.4	1212.8	1901.4	1680.2	1275.0	1927.1	1707.3	1286.4
3.5	1801.4	1574.6	1230.6	1921.4	1701.3	1283.9	1943.5	1724.5	1293.7
4	1831.4	1606.3	1243.9	1936.4	1717.1	1290.6	1955.7	1737.5	1299.1
4.5	1854.8	1630.9	1254.3	1948.1	1729.4	1295.8	1965.2	1747.5	1303.4
5	1873.4	1650.6	1262.6	1957.4	1739.3	1299.9	1972.9	1755.6	1306.8
5.5	1888.7	1666.8	1269.4	1965.1	1747.4	1303.3	1979.1	1762.1	1309.5
6	1901.4	1680.2	1275.0	1971.4	1754.1	1306.1	1984.3	1767.6	1311.8

Table-3. melting temperature numerical values of the geometric shape dodecahedron, icosahedron, cub octahedron for gold, platinum and palladium**.** (from Eq 6)

D	$T_m(D)(K)$								
	dodecahedron			icosahedron			cub octahedron		
	Pt	Pd	Au	Pt	Pd	Au	Pt	Pd	Au
.5	1733.4	1502.9	1200.3	1587.6	1349.0	1135.5	1414.4	1166.2	1058.5
1	1887.4	1665.4	1268.8	1814.5	1588.5	1236.4	1727.9	1497.1	1197.9
1.5	1938.8	1719.6	1291.6	1890.2	1668.3	1270.0	1832.4	1607.4	1244.3
2	1964.4	1746.7	1303.0	1928.0	1708.2	1286.8	1884.7	1662.5	1267.6
2.5	1979.8	1762.9	1309.9	1950.7	1732.2	1296.9	1916.0	1695.6	1281.5
3	1990.1	1773.8	1314.4	1965.8	1748.1	1303.6	1936.9	1717.7	1290.8
3.5	1997.4	1781.5	1317.7	1976.6	1759.5	1308.4	1951.9	1733.4	1297.4
4	2002.9	1787.3	1320.1	1984.7	1768.1	1312.0	1963.1	1745.2	1302.4
4.5	2007.2	1791.8	1322.0	1991.0	1774.7	1314.8	1971.8	1754.4	1306.3
5	2010.6	1795.4	1323.6	1996.1	1780.1	1317.1	1978.7	1761.8	1309.4
5.5	2013.4	1798.4	1324.8	2000.2	1784.4	1318.9	1984.4	1767.8	1311.9
6	2015.8	1800.9	1325.8	2003.6	1788.0	1320.4	1989.2	1772.8	1314.0

4. Conclusion

In the end, we can say that thermodynamics properties can create good vision on Nano science, particularly in catalyst. Future advances in catalyst depend to the ability of control the size and shape of the nanoparticles.

Therefore we see that the shape of nanostructure that has low surface to volume ratio is more stable. Then we can conclude that in Nano scale, crystals have the lowest stabilities.

We found that Dodecahedron melting temperature has the lowest variations in the greater sizes and variations of tetrahedron melting temperature is the greatest in the Smaller sizes. Then in general the Dodecahedron and tetrahedron geometry are the most and the least stable respectively.

Also another result can be concluded from the tables is that melting temperature variation of Au nano catalyst is lower than the others but melting temperature variation of Pd nano catalyst is more. We can say that Pd-Pt is more economical catalyst from the others.

Because little experiments has been done in this field trials, it is required that doing experiments to determine the accuracy of our Statements.

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