Effects of temperature and sulphur on the composition profile of Pt-Rh nanocatalysts: A comparative study.

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Abstract
Monte-Carlo simulation technique has been used to investigate the effect of temperature and adsorbed gases on the composition profile of unsupported Pt-Rh nanocatalysts. For a 2406 atom fcc cubo-octahedral Pt\textsubscript{50}Rh\textsubscript{50} nanocatalyst the shell-wise composition for all the eight shells has been simulated. For the temperatures 700 K, 1000 K and 1300 K, the top shell of clean Pt-Rh nanocatalysts is found to be mildly Pt-enriched, while the second shell is Pt-depleted. The Pt concentration of the top shell shows a maximum at $T = 1000$ K. In presence of a quarter monolayer of adsorbed oxygen the top shell shows Rh enrichment, while all the other shells show Pt-enrichment. This is true for all the three temperatures for which the composition profiles have been studied.

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1. Introduction

The ceria-supported Pt-Rh bimetallic catalysts have been found to be very effective three-way catalysts for simultaneous elimination of the CO, NO and the hydrocarbons from automobile exhaust gases [1-3]. These catalysts are increasingly used globally in the catalytic converters of automobiles. It is important, therefore, to have a thorough understanding of the structural, electronic and catalytic properties of these catalysts. In this work, we present the results of our theoretical investigations on the composition profile of unsupported Pt-Rh bimetallic nanostructures as a function of temperature and adsorbates.

The structural and catalytic properties of the Pt-Rh alloy surfaces have earlier been exhaustively studied by several groups [4-11]. Van Delft et al. [4] used AES to investigate the Pt$_{62}$Rh$_{38}$ and Pt$_{10}$Rh$_{90}$ alloy systems. They found a surface enrichment with Pt for both the systems. When studied as a function of temperature this surface enrichment showed a maximum at about 1000 K for both the systems. This phenomenon was explained in terms of a vibration entropy contribution to the enthalpy. Tsong et al. [5] made a layer-by-layer analysis of a Pt-Rh alloy tip at 1000 K to show that the topmost layer is Pt-enriched and the second layer is Pt-depleted. The distribution of Pt and Rh atoms depend on the annealing temperature. Hirano et al. [6], on the other hand, showed that the presence of adsorbates like oxygen and/or nitric oxide has a more pronounced effect on the chemical restructuring process of the Pt-Rh surface layers than the annealing temperature. While there have been a large number of theoretical studies on this segregation phenomenon in clean and gas-covered alloy surfaces [4-7], the number of segregation studies for supported particles are comparatively few. Some theoretical investigations for Pt-Rh particles have been made by Strohl and King [8], Schoeb et al. [9] and Yang et al [10]. These works are based either on rigid-lattice Monte-Carlo (MC) simulations or on molecular dynamics / Monte-Carlo-correlated ef-
ffective medium theory, where the interaction energies were generated from a simplified version of the non-selfconsistent electron-density-functional correlated effective medium (CEM) theory [11]. For the fcc cubo-octahedral particles the atomic distribution at the corner, edge and fcc(100) and (111)-like faces were obtained as a function of the particle size and composition. A shell-by-shell composition profile of the particles were not, however, studied in these works. It is the main purpose of the present work to investigate the shell-wise composition of Pt-Rh nanoparticles as a function of temperature and adsorbate coverage. For the 2406 fcc cubo-octahedral Pt-Rh nanoparticles a Monte-Carlo simulation has been carried out to analyse the atomic distribution in top few layers. We show that the presence of adsorbate like oxygen drastically changes the composition profile, while the effect of temperature from 700K-1300 K on the composition profile is relatively much small. These studies are useful in understanding the structure and catalytic properties of ceria-supported Pt-Rh catalysts used in the catalytic converter. The plan of the paper is as follows. In section 2, the theoretical model developed earlier and used in the present work is briefly outlined. The results for clean and oxygen-adsorbed Pt-Rh nanoparticles are presented in section 3. The conclusions are drawn in section 4.

2. Theoretical model

The theoretical model used in this work is the MC simulation technique employed elsewhere in connection with surface segregation in presence and in absence of adsorbed species[12-16]. One determines the pair-bond energy between two nearest neighbour atoms $E_{ij}$ in the form

$$E_{ij} = \frac{w_{ij}}{Z} + E_{ic}^i(n)/n + E_{ic}^j(m)/m \quad (1)$$

where the indices i and j are the component metals A or B of the bimetallic system AB.
and \( w_{ij} \) is the interchange energy for two dissimilar atoms. \( w_{ij} = 0 \) if \( i = j \) and this interchange energy is related to the excess heat of mixing. \( Z \) is the bulk coordination number. \( E_{ci}^{i} (n) \) is the partial bond energy of the \( i \)-atom with \( n \) nearest neighbours etc. Usually, the coordination-dependent partial bond energy, \( E_{ci}^{i} (n) \) (for \( n = 2 - 12 \)), is calculated from an empirical formula like

\[
E_{ci}^{i}(n) = a^i + b^i n + c^i n^2
\]

where \( a^i, b^i \) and \( c^i \) are adjustable constants that can be derived from experimental data of dimer energy, surface energy and the cohesive energy of a metal corresponding to \( n=2, 8 \) and 12 respectively. Once the pair binding energy \( E_{ij} \) is evaluated it is the usual MC procedure to compute the configuration energy for a particular distribution of A and B atoms in the nanoparticle. And from various such distributions an equilibrium distribution may be found giving the shell-wise occupation of sites by A or B atoms. In presence of adsorbates, there are additional energy terms to describe the chemisorptive bond and the concomitant metal-metal pair-bond energy variations. King and Donnelly [12] showed that since in Monte-Carlo simulations only the differences in energies are calculated, it is sufficient to add the difference in chemisorption energy of the adsorbate on the two metals to the configuration energy. This has been done in this work to study the role of adsorbed oxygen on the composition profile.

3. Results and Discussions

We are interested in the composition profile of the outer shells of the Pt-Rh nanoparticles since it is only the outer shells which are important in catalysis and can be influenced by adsorbed atoms. For convenience, we avoid the usual description of shell structure where the shells are constructed by atoms equidistant from the centre. As may be found from the work of Yang and DePristo [10] that to describe a 200-atom
fcc cubo-octahedral particle one needs 11 shells. This concept may be very useful for describing the stability and morphological structure of a nanoparticle. However, for a large fcc cubo-octahedron particle of 2406 atoms as considered in this work this description would require a large number of shells which is very difficult to handle. In our treatment, the outermost shell (we also call it ‘top shell’) comprises all the atoms at the corner sites, bridge sites, fcc(100) and fcc(111)-type faces. The total number of such atoms is 752. If we peel off these atoms from the outermost shell, the second shell would be exposed to the adsorbed gases. The number of atoms in the second shell is 582. In this way, we may have just eight shells with total number of atoms in the shells (counting from the outermost shell inward) as 752, 582, 432, 302, 192, 102, 38 and 6 respectively. The number of Pt and Rh atoms are counted in each shell and the fraction of these atoms in the shells are calculated. In this work we have calculated the fraction of Pt and Rh atoms for a bulk Pt$_{50}$Rh$_{50}$ particle.

The values of the parameters used for the present MC simulation are the following:

Pt: $a = -0.4287398$, $b = -0.0474969$, $c = 0.0035483$ , $E_{ad}$(O) = 85 kJ/mole

Rh: $a = -0.4744544$, $b = -0.0341727$, $c = 0.0028138$ , $E_{ad}$(O) = 102 kJ/mole

and $w_{ij}/Z = -0.00691$ eV. $E_{ad}$(O) is the chemisorption energy of oxygen atom on the metal.

We have calculated the composition profile for $T = 700$ K, 1000 K and 1300 K. The studies at $T = 700$ K is of particular importance since the exhaust temperature at the three-way catalyst is of this order. To study the effect of adsorbed gases we have considered one coverage ($= 0.25$) of adsorbed oxygen. This is because it is the presence or absence of oxygen that controls the CO oxidation and NO reduction in three-way catalysts. The calculation, however, can easily be repeated for other coverages and other adsorbed gases. The present work attempts to study the qualitative change of composition profile as a function of temperature and adsorbate coverage.
Figure 1 shows the % of Pt atoms in top four shells. The top shell (shell number 1) corresponds to the surface layer and shows Pt-enrichment for all the three temperatures; while the second and third shell shows Pt-depletion for the three temperatures. The no segregation line is represented by the dots. The behaviour from shell number 4 to higher (moving towards the core of the particle) is divergent. However, for surface and catalytic properties the top 2-3 shells are of real interest since they constitute the surface layers. Besides, the top shell for a 2406-atom particle represents 31% of total atoms, sometimes known as dispersion; while the top 2, top 3 and top 4 shells represent 55%, 73% and 86% of total atoms for this particle respectively. If we compute the % of Pt atoms averaged over top 2, top 3 and top 4 shells, the results would be as shown in Figure 2. The results are computed for all the three temperatures. The results averaged over all the eight shells would, of course, be the bulk Pt concentration which is 50%. This is why all the curves meet at shell number 8. It may be noted that for T = 700 K the top shell is Pt-enriched; but the averages over top 2, top 3 and top 4 shells show Pt-depletion. For T = 1000 K and 1300 K, however, the averages over top 2, top 3 and top 4 shells show Pt-enrichment. This signifies that the properties, that depend on the composition of the top shell only, would not change with temperature, since the shell is Pt-enriched. However, the properties that depend on the average composition of top 2, top 4 or top 4 shells will change with temperature. In Figure 3 we plot the same shell-averaged Pt concentration as a function of temperature. In addition to the features described above for Figure 2, an important feature becomes obvious in figure 3. It is that the Pt-enrichment shows a maximum at T = 1000 K. This result agrees very well with the experimental findings of Vandelft et al. [4] for the polycrystalline alloy surface. The authors [4] explained this behaviour with a surface segregation model containing both enthalpy and vibrational entropy contribution. It is likely that for the present system of nano-sized Pt-Rh particles also the entropy contribution may
be responsible for the temperature dependence of surface segregation. In Figure 4 we plot the % of Pt atoms in presence of 0.25 monolayer of adsorbed oxygen and compare them with the results for clean system, shown already in Figure 1. It may be noticed that the presence of 0.25 monolayer of oxygen has a very strong effect on the composition of the top shell as well as on other shells. Because of higher binding energy of oxygen on Rh compared to that on Pt the Rh atoms are pulled to the top shell at all the three temperatures. This segregation is so strong that the rest of the shells of the particle become Pt-enriched. On comparing the effect of temperature and adsorbates on the shell composition it may be noted from Figure 4 that the effect of temperature on the composition profile is mild. This is obvious from the spreadth of the composition for three temperatures in both the clean and adsorbed cases. However, the large separation of the two sets of curves (each set consisting of the results for three temperature), one for the clean case and the other for the oxygen-adsorbed case, signifies that the effect of adsorbates is much stronger on the composition. We believe, these results can be exploited in the three-way catalyst where Rh acts as the main component in reducing NO. Furthermore, it may be mentioned that the present study considers one bulk composition and one coverage of one adsorbed species. This may be repeated for other compositions, adsorbates and coverages as the situation demands.

4. Conclusions
A Monte-Carlo procedure has been utilised to compute the atomic composition of a Pt-Rh nanoparticle in the form of shells gradually peeled off from the outer layer. The composition profile correctly predicts Pt segregation in the top layer; but the variation of the composition of the outer shells with temperature is small. In contrast, the variation of the composition of the shells with presence of adsorbed oxygen is very large.
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Figure Caption

Fig. 1. MC-simulated % of Pt atoms in different shells of a 2406-atom Pt$_{50}$Rh$_{50}$ nanoparticle for different temperatures.

Fig. 2. MC-simulated average % of Pt atoms in top, top 2, top 3 and top 4 shells of a 2406-atom Pt$_{50}$Rh$_{50}$ nanoparticle for different temperatures.

Fig. 3. MC-simulated average % of Pt atoms in top, top 2, top 3 and top 4 shells of a 2406-atom Pt$_{50}$Rh$_{50}$ nanoparticle plotted as a function of temperature to demonstrate the existence of a maximum at T = 1000 K.

Fig. 4. MC-simulated % of Pt atoms in different shells of a clean and oxygen-adsorbed 2406-atom Pt$_{50}$Rh$_{50}$ nanoparticle.
Average % Pt atoms in shells

shell number

T = 1300 K

T = 1000 K

T = 700 K
Average % Pt atoms in shells vs Temperature (in K)

- Top 4 shells
- Top 3 shells
- Top 2 shells
- Top shell

Temperature (in K): 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400

Average % Pt atoms in shells: 48, 50, 52, 54, 56
