The importance of CeO$_2$ support in three-way catalysts Pt-Rh/CeO$_2$ used for controlling pollution from automobile exhaust gases is well established$^{15}$.

CeO$_2$ acts as an oxygen storage component, stabilises $\gamma$-Al$_2$O$_3$, promotes water gas shift activity and stabilises Pt and Rh dispersion. CeO$_2$ has also been known to promote CO oxidation activity by reducing the activation barrier for CO oxidation$^{56}$. It has also been observed that reduction of the Pt$^{4+}$ and Rh$^{3+}$ is more facile when in contact with CeO$_2$.$^{7,8}$. Particularly, coupling the Pt, Rh with CeO$_2$ shows reduction at lower temperature than when they are independently reduced. Such synergism was proposed to be responsible for enhanced oxygen storage by the catalysts$^{6}$. In this work we consider the effect of this synergistic reduction on the composition of Pt-Rh nanocatalysts. However, our theoretical model used to study this effect does not consider the complicated experimental reduction procedure. Rather, we want to study in a simplistic way what happens when the Pt-Rh catalysts on ceria or on ceria/alumina are reduced in hydrogen at temperatures (say) 700-1000 K, relevant to real catalytic reactions in three-way catalysis.

The principle behind this work is the following: CeO$_2$ is a weak semiconducting support which is of redox type than of acidic or basic nature. On reduction of Pt$^{4+}$ and Rh$^{3+}$ with CeO$_2$ or CeO$_2$/$\gamma$-Al$_2$O$_3$, Ce$^{3+}$ ion may gain an electron to become Ce$^{3+}$ ion and CeO$_2$ becomes CeO$_{2-x}$. On further reduction, in principle, the ion may get more electron and ultimately one may have the Ce metal atoms. The metal-support interaction, in this gradual reduction process, may change from a weak metal-semiconductor type interaction to a stronger metal-metal type interaction. This may cause a change in the surface composition of the Pt-Rh catalysts. We use in this work a Monte-Carlo (MC) simulation procedure to study how the composition of fcc cubo-octahedral Pt-Rh nanocatalysts of several sizes changes in the top shell of the particle due to this metal-support interaction. We also find the composition profile of a few layers above the support. While the overall surface composition of the top shell of the Pt-Rh nanocatalysts is important in controlling the activity of the catalysts, the composition in the layer in contact with the support would show an atomistic picture of the effects of metal support interaction and hence of the degree of reduction of Pt-Rh/CeO$_2$ on the basal plane.

**Theoretical Model**

In our earlier work we studied the segregation behaviour of the free Pd-based nanoparticles by using the Monte-Carlo (MC) simulation procedure$^{9,12}$. In this work, we take into account the effect of gradual reduction of Pt$^{4+}$ and Rh$^{3+}$ with CeO$_2$ or with CeO$_2$/$\gamma$-Al$_2$O$_3$ through the metal support interaction to know how this surface distribution changes with the base atoms interacting with the support. When the ceria support is semiconducting the metal-support interactions are weak. When the support is fully reduced the metal-support interactions are strong. In this work, we consider the strengths of the metal-support interactions between these two extremes.
This helps us to understand how the strength of the metal-support interaction changes the fraction of metal components of the Pt-Rh nanocatalysts at the base layers and in the top shell of the particle. This, in turn, may throw light on the role of the metal support interaction on the rate of different catalytic reactions.

The details of the MC model are given elsewhere. For accurate computation of the configuration energy in our MC simulation procedure the pair bond energies are considered dependent on the coordination number of the atoms. The pair bond energy between two nearest neighbour atoms, \( E_{ii} \), is related to the site energy \( E_{c} \) etc. as:

\[
E_{ii} = \frac{a_i + b_i n + c_i n^2}{n} \quad \ldots \quad (1)
\]

where \( i, j = A \) or \( B \) atom of the general \( A_1 B_{1-x} \) bimetallic system and \( w_{ij} = 0 \) if \( i = j \). \( E_{c} \) is the cohesive energy of the i-atom with n nearest neighbours etc. \( w_{ij} \) is the interaction energy for two dissimilar atoms which may be estimated from the excess heat of mixing; and \( Z \) is the bulk coordination number. In order to find \( E_{c} \) an empirical formula is given:

\[
E_{c} = \frac{a' + b'n + c'n^2}{n} \quad \ldots \quad (2)
\]

is used where \( a', b' \) and \( c' \) are constants for the i-metal and may be obtained from the experimental values of the dimer energy, the surface energy and the energy for monovacancy formation.

For the metal support interaction, \( V_{ms} \), which is a measure of the degree of reduction, we have to consider the ceria-Pt interaction and ceria-Rh interaction. Since in the MC simulation for this problem it is only the difference in energy between ceria-Pt and ceria-Rh interactions that comes into play we consider the difference in metal-support interaction [\( V_{ms} \) (Pt)-\( V_{ms} \) (Rh)] as \(-0.01 \) eV, \(-0.05 \) eV and \(-0.08 \) eV. The last value \(-0.08 \) eV is the difference between Ce-Pt and Ce-Rh bond energies. This is the energy when the support is fully reduced and the support has reduced Ce metal component. And the metal-support interaction becomes mainly metal-metal interaction and is the strongest. The first two values, [\( V_{ms} \) (Pt)-\( V_{ms} \) (Rh)] = \(-0.01 \) eV, \(-0.05 \) eV are arbitrarily chosen lower in strength than \(-0.08 \) eV.

Now, once the constants \( a', b' \) and \( c' \) are derived and the parameters \( w_{ij}/Z \), and [\( V_{ms} \) (Pt)-\( V_{ms} \) (Rh)] are provided, the MC simulation is carried out in the usual manner.

**Results and Discussion**

In this work we have several external control parameters like temperature, overall composition and the size of the nanocatalysts. Only one temperature, namely \( T = 700 \) K is considered here. This is the temperature very much relevant for catalytic reactions in three-way catalysts. For this work again we consider the Pt50Rh50 composition. This will give a quick demonstration of the effect we want to study, namely, the composition change due to reduction or metal-support interaction. Lastly, the simulation is carried out for three sizes of the fcc cubo-octahedral catalysts with total number of atoms, \( N \), being 586, 1289 and 2406.

In order to understand the effect of gradual reduction of Pt-Rh ceria/alumina and hence the metal support interaction on the composition profile of the nanocatalysts, three strengths of metal-support interaction mentioned earlier in addition to \( V_{ms} = 0 \) are considered. With the above sets of parameters it is now possible to simulate the composition profile of the Pt-Rh nanocatalysts. The input parameters for MC simulation as described by Eqs (1) and (2) and used in this work are given in Table 1. The exchange energy, \( \omega_{Pt,Rh} = -0.00691 \) eV.

Figure 1 shows schematically the Pt and Rh atoms at the basal layer of a 586-atom fcc cubo-octahedral.
Pt$_{50}$Rh$_{50}$ nanocatalyst as a function of the strength of metal support interaction, $V_{me}$.

In Fig. 2 we show how for different sizes of Pt$_{50}$Rh$_{50}$ nanocatalysts Pt fraction at the base layer in contact with the ceria support and at the three layers above the basal layer change with the strength of metal support interaction. In the X-axis, the number 1 corresponds to the base layer of the catalyst in contact with the support; and the numbers 2, 3 and 4 denote the layers above the base layer. In all the figures, the dotted line shows the no segregation line for the Pt$_{50}$Rh$_{50}$ systems. From the Figs 2(a), (b) and (c) several features become evident. First, at the basal layer of the catalyst (layer in contact with the support and index number 1) the Pt fraction increases with the strength of the metal support interaction and hence with the degree of reduction of the Pt-Rh/ceria/alumina sample. This is true for all the particle sizes. Secondly, at the second, third and fourth layers the Pt fraction for all the particle sizes varies with the strength of metal support interaction, but without any general trend for this variation. However, the divergence of this variation gradually diminishes at the fourth layer tending to reach the article-average of 50-50 composition. When the Pt fraction in the basal layer is plotted as a function of the metal support interaction the results look like as shown in Fig. 3. It may be noticed that for all the particles the Pt fraction increases with strength of metal support interaction, but the Pt fraction is highest for $N_T = 586$. For metal-support strength between $-0.01$ eV to $-0.08$ eV the Pt fraction is more than 50% for all the particles. However, the Pt fraction for $N_T = 1289$ is found to be minimum amongst the three particle sizes. The results for Pt fraction at the basal layer, plotted as a function of $N_T$ for various strengths of metal-support interaction are shown in Fig. 4, which clearly show a dip near $N_T = 1289$. The importance of these results showing the Pt fraction at the basal layer or a few layers above the basal layer as shown in Figs 1-4 lies in the fact that the Pt fraction on the particle surface exposed to the reacting gases will depend on how many Pt or Rh atoms are in the basal layers, since these are finite nanoparticles and mass balance equation has to be ensured. It is the fraction of the Pt or Rh atoms in the exposed surface of the nanoparticles which take part in catalytic reaction. Therefore depending on the degree of reduction and hence the strength of metal-support interaction the Pt or Rh atoms on the catalyst surface will control the catalytic activity.

Fig. 2—MC-simulated Pt fraction of fcc cubo-octahedral Pt$_{50}$Rh$_{50}$ particles at the base and three layers above the base for different strengths of metal support interaction. (a) $N_T = 586$; (b) $N_T = 1289$; (c) $N_T = 2406$. The dotted lines are no segregation lines.
In Fig. 5 the Pt fraction in the exposed surface is shown. This includes all surface atoms of the nanoscopic except the atoms at the basal layer with coordination number 8. It may be mentioned here that the atoms at the basal layer with coordination 6 and 7 correspond to the corner and edge atoms respectively; and they are exposed to the reacting gases. The results shown in Fig. 5 for the three particle sizes show an interesting property. There is wide variation in the Pt fraction of the exposed surfaces. These differences may be exploited for desired catalytic activity and selectivity in reactions. What is inferred from Fig. 5 is that the sample preparation under reducing condition may be manipulated to give desired particle size, which in turn controls the Pt or Rh fraction of catalyst surface. Since the activation barriers and the rates of different reactions of importance in pollution control like CO oxidation, NO reduction etc. depend on the surface composition, the present simulated results may be of use in understanding the above reactions on Pt-Rh/ceria catalysts.

To conclude, the gradual reduction of Pt\(^{3+}\) and Rh\(^{3+}\) with CeO\(_2\) or CeO\(_2\)/Al\(_2\)O\(_3\) catalysts and the change in the metal-support interactions are correlated. Through the MC simulation studies of the role of metal-support interaction on the surface composition of Pt-Rh nanocatalysts, it has been shown that—

(i) the base of the Pt-Rh nanocatalysts gets enriched with Pt and increases with the strength of the metal support interaction; and

(ii) the Pt fraction of the exposed surface of the Pt-Rh nanocatalysts is large for weak metal-support interaction, but decreases with strength of metal-support interaction.

References